

Physics, Chemistry and Application of Nanostructures

Reviews and Short Notes to Nanomeeting 2003



Editors

V. E. Borisenko
S. V. Gaponenko
V. S. Gurin

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Reviews and Short Notes to Nanomeeting 2003**

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INTERNATIONAL CONFERENCE

NANOMEETING-2003

Minsk, Belarus, May 20-23, 2003

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FOREWORD

The first years of the XXI-st century have brought new fundamental knowledge and novel applications of nanostructures. Nanoelectronics and nanophotonics, bioinformatics and molecular electronics are extensively progressing on the basis of recent achievements in nanotechnology. The results obtained are discussed at *NANOMEETING-2003* (20-23 May, 2003), which is the International Conference on Physics, Chemistry and Application of Nanostructures traditionally organized each two years in Minsk (Belarus).

The book that you keep in your hands collects invited reviews and short notes of contributions to *NANOMEETING-2003*. The papers in the book are arranged in traditional sections: Physics of Nanostructures, Chemistry of Nanostructures, Nanotechnology and Nanostructure Based Devices. Both basic and applied researches are presented. Among different results characterizing our knowledge about the nanoworld, one can note an increased interest to Ge/Si quantum dot systems, photonic crystals, carbon nanostructures, biological molecules, self-scrolled semiconductors, epitaxial GaAlN onto Si. Their indeed astonishing properties promise a birth of novel approaches to information processing. Scanning probe techniques and nanochemistry, self-organization and self-assembling have got new impetus to be applied in nanotechnology. The examples can be found in the book. The style of the presentations has been mainly preserved in its original form.

We deeply acknowledge Sponsors provided the financial support for the Conference.

Victor E. Borisenko
Francois Arnaud d'Avitaya
Co-chairmen of *NANOMEETING-2003*

Minsk and Marseille
January 2003

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PHYSICS OF NANOSTRUCTURES

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Si/SiGe NANOSTRUCTURES: CHALLENGES AND FUTURE PERSPECTIVES

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Embedding SiGe and Ge quantum structures into the Si host crystal opens up new paths for the integration of ultra fast electronic and opto-electronic devices into the mature Si micro-electronics. In this paper some of these paths are discussed and the challenging problems of materials research are addressed. Special emphasis is put on the Dot-FET concept and on the possibility of light emission from Si/SiGe quantum structures.

1 Introduction

In 1952 H. Welker discovered the semiconducting properties of III/V compounds [1], leading to a lot of enthusiasm about future applications. Today, these materials dominate clearly the market for opto-electronic devices and are widely used for high speed microelectronics [2,3]. In fact, the appearance of III/V semiconductors was an additional stimulation for the development of ever faster and smaller Si devices. In particular, the concept of hetero- and quantum well structures opening the field of band gap engineering, was extremely fruitful for the progress of III/V opto-electronic and high frequency devices [4]. With the introduction of SiGe this path became also available for the Si technology. The invention of the Si/SiGe hetero-bipolar transistor (HBT), allowed the design of Si based high frequency devices and HBTs exceeding transit frequencies of 200 GHz have been realized [5]. These devices now enter the domain of wireless communication technology, even though for high end applications III/V devices are still superior [6]. More recently, Si channels with tensile strain embedded in a relaxed SiGe lattice draw a lot of attention, due to the high electron mobility in the strained Si and the potential compatibility with Si CMOS technology [7]. Thus, SiGe technology has entered the roadmap for the development of future generations of Si microprocessors. However, several obstacles have to be circumvented before this technology may become available. Typically, a heavily dislocated SiGe buffer layer is introduced to account for the lattice mismatch between the Si substrate and the relaxed SiGe film, which carries the strained Si layer [8]. The high amount of threading dislocations, the reduced thermal conductivity of SiGe compared to Si and the necessity to integrate p- and n-type devices on the same chip certainly are challenging problems for this technology.

Si is an indirect semiconductor, thus not suitable for the fabrication of optoelectronic devices. Adding optical functionality to Si microelectronics is one of the most challenging problems but may revolutionize communication technology [9,10]. The key device would be an efficient emitter, i.e. a laser.

In this paper the potential to address some of these obstacles and challenges by using Ge quantum dots and Si/SiGe quantum well structures are discussed with respect to applications in micro- and optoelectronics.

2 Perspectives of Ge quantum dot structures

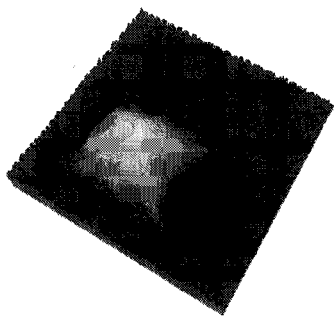


Figure 1. STM image of a 60x60 nm Ge hut cluster deposited by MBE at 520°C.



Figure 2. TEM micrograph of stacked Ge islands imaging the strain fields.

Ge dots on Si (100) assemble via the Stranski-Krastanov mode of growth. Typically, two shapes can be distinguished, “hut” cluster with a square or elongated shape and (105) side facets [11,12] and multiple faceted “dome” cluster [13]. The latter ones occur typically at higher temperatures and Ge coverages than the hut cluster. High densities and small cluster sizes are achieved at deposition temperatures $< 500^{\circ}\text{C}$. Depending on the growth temperature, the diameter of Ge islands can be controlled in the range from 15-300 nm. If pre-deposition of C is used smaller sizes are possible and the temperature dependence is relaxed [14]. Fig. 1 shows a typical in-situ STM image [15] of a Ge hut cluster deposited by molecular beam epitaxy (MBE) at 520°C using 4.8 ML of Ge. The size of this island is about 60x60 nm. These islands harbor a complex strain distribution [16]. The top of the islands is largely relaxed exhibiting a larger than Si lattice constant. Consequently, after embedding the islands in Si by overgrowth, the Si in the vicinity of the dot is strained. The strain field is easily visible in the cross sectional TEM micrograph presented in Fig. 2. The image shows two islands stacked on top of each other. The strain field induces the nucleation of the second

island on top of the first [17].

Remarkably, the size of these Ge islands is in the range of the gate length and width of next generation CMOS transistors [7]. Accordingly, it has been proposed to use the strained Si on top of islands to create a channel for electrons and the Ge island itself to create a channel for holes [18]. This concept of a dot based field effect transistor (Dot-FET) would harbor fast p- and n-type devices on the same

structure. In addition, since no relaxed SiGe buffer layer is needed, the related problems due to the high threading dislocation density and the low thermal conductivity of relaxed SiGe buffers can be circumvented. The use of Ge dots in FETs requires exact positioning of ordered dots at preset locations. Recently, it has been demonstrated that by using shallow grooves such a positioning of individual dots is possible [19].

Further constrains of this concepts may arise from the non-uniformity of the strain field above the dots. So far only limited knowledge about the size, the uniformity and the strength of the strain fields induced by Ge dots is available. Certainly the lateral dimensions of the Ge dots have to exceed the dimensions of the gate of the transistor. It is well known, that Ge dots intermix during the overgrowth with Si, leading to a shape transformation by transporting material from the top to the pedestal of the dot [20]. It can be expected that this shape transformation leads to an increase in the uniformity of the strain field on top of the dot, but at the same time the intermixing reduces Ge concentration of the dot and thus lowering the strain in the Si cap. Future research has to focus on the relation between shape and strain fields of Ge dots and the impact of non-uniformity strain distributions within the channel on the performance of the device. Certainly dots having a high Ge concentration and thus inducing strong strain fields and providing rather uniform strain fields at the same time would be most beneficial.

Currently detailed studies on the intermixing during the early states of overgrowth of Ge dots by Si are performed. The intermixing can be reduced by lowering the growth temperature or by using a surfactant. In the latter case, growth was interrupted after the Ge dot deposition (720°C) and the sample was transferred to a neighboring chamber equipped with a hydrogen plasma source. The surface was covered with H and than growth was resumed in the MBE chamber at 500°C. Fig. 3 shows a cross sectional TEM of this sample exhibiting a Ge island of nearly 300 nm in diameter and 30 nm in height. The island preserved the shape of a dome cluster, as indicated by the still present facets, suggesting that no intermixing occurred during the overgrowth. It can be predicted that such an island induces a strong strain field in the Si cap layer.



Figure 3. Ge dome cluster embedded in Si using a H surfactant layer.

Fig. 4 shows STM views of Ge islands during the early stages of Si overgrowth, a) uncapped dots, b) after 1 monolayer (ML) and c) after the deposition of 5 ML of Si at 300 and 340°C respectively. The uncapped sample exhibits dome and hut cluster. The islands preserve their shape after a capping of 5 ML, in contrast to experiments performed with an overgrowth temperature of 620°C [20]. However, after the deposition of 1 monolayer of Si a new type of small quadratic islands occurs, which is rotated by 45° in comparison to the normal Ge hut cluster. It is assumed that these islands consist of Si and that at these low temperatures the Si does

not intermix with the Ge islands or Ge wetting layer. Most likely Si does not wet Ge uniformly and 3-dimensional growth occurs. The lack of intermixing for low temperature overgrowth is also indicated by photoluminescence (PL) spectra [21]. Dot structures emitting at energies < 650 meV indicate the presence of Ge islands under compressive strain with a Ge concentration close to 100%. The strong confinement of holes in these islands opens a new path to enhance the luminescence efficiency of Ge quantum dots for opto-electronics.

The realization of a Ge Dot-FET requires exact alignment of the gate on top of

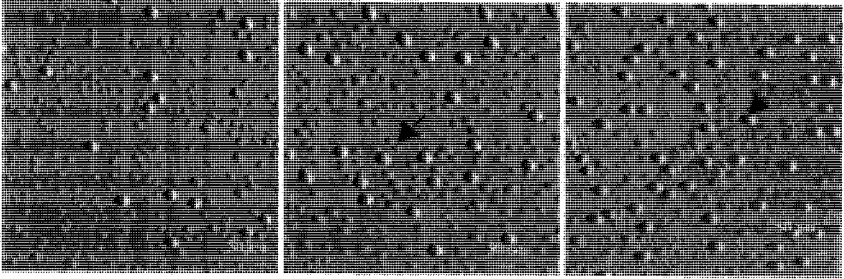


Figure 4. STM images of Ge dome and hut cluster deposited at 620°C and over-grown with a) 1 ML, b) 3 ML (300°C) and c) 5 ML (340°C) of Si. Black arrows point to cluster, which are rotated by 45° with respect to Ge hut clusters.

the buried Ge dot. This might be achieved by a self alignment using the effect of vertical stacking of Ge islands as illustrated in Fig. 2. The self alignment of gates may be obtained as follows. On top of the structure a layer of uncapped Ge islands is deposited, which align to the buried islands. Next, a sacrificial layer is evaporated under shallow angles, leaving a side facet of the surface dots uncovered. The Ge dots can be selectively etched opening up windows for the gate stack deposition. The gate layers can be lifted from the field areas by etching the sacrificial layer [22].

3 Perspectives of Si/SiGe quantum well structures

In this chapter the focus is put on novel application for Si/SiGe quantum well structures aside from the applications in CMOS and HBT devices discussed in the introduction and references therein.

3.1 Self scrolling Si/SiGe micro- and nanotubes

The scaling down of sizes for high speed, large integration Si microelectronic devices not only puts constraints on transistors, but also on capacitors and coils, which are up to now rather spacious devices. The self scrolling process of strained layer hetero- and quantum well structures [23,24] offer routes to considerably reduce the area consumed by these devices. The self-scrolling of strained bilayers has been

demonstrated for III/V as well as for Si/SiGe films. The concept is schematically illustrated in Fig. 5. The structure consists of an undoped Si film and a p^{++} SiGe/Si bi-layer. The thickness of Si and SiGe as well as the Ge concentration determines the diameter of the tube. Typically film widths of 1-100 nm at a Ge concentration of 10-40% have been used in our experiments [25]. For applications as capacitors or coils, the bilayers have to be additionally coated with an insulating and/or a metal layer. Here we introduce a simple process to fabricate Si/SiGe/Cr nanotubes.

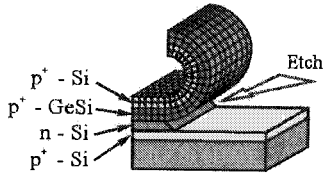


Figure 5. Schematic view of the self-scrolling process of SiGe/Si bi-layer (Fig. courtesy of V. Prinz).

The pseudomorphic $\text{Si}_{0.8}\text{Ge}_{0.2}/\text{Si}$ (12/50 nm) heterostructure heavily doped with boron ($5 \cdot 10^{19} \text{ cm}^{-3}$) was grown on a (001) n-type Si-wafer at 400°C by MBE. Afterwards, a 20-nm thick chromium layer was evaporated onto the structure. The choice of chromium as an upper-layer material was motivated by the fact that the use of this metal for preparing electron-beam lithography masks represents a well-established technology, and chromium is stable to alkaline etchants, harboring simultaneously high internal stress when deposited onto silicon. Electron lithography was used to define a pattern on the surface of the initial planar structure. Fig. 1 illustrates the mask used. After the resist has been developed the pattern was transferred into the underlying SiGe/Si/Cr film using C_2F_4 and SF_6 reactive ion etching (RIE). Next, the structure was dipped into KOH to form defined facets. This dip is very crucial, since it determines from which side of the mesa the structure starts to scroll during the dip in the subsequent etch in the aqueous 3.7% NH_4OH solution. Without the dip the result would be a ring like structure.[25].

The correct orientation of the mesa and the dip in the KOH etch leads to the formation of a (111) facet along the short side of the mesa. The (111) facet is not attacked by the selective etch and thus the scrolling is initiated from the long side. The highly strained SiGe/Si/Cr structure is detached from the substrate. The Cr film

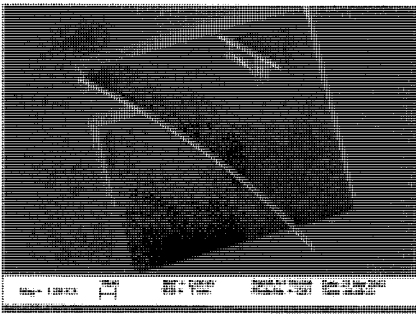


Figure 6. Free standing, $>200 \mu\text{m}$ long Si/SiGe microtube, $\varnothing 4 \mu\text{m}$.

deposited onto Si is under tension, while the SiGe layer is under compression. As a result, the free-standing SiGe/Si/Cr structure undergoes bending due to the internal elastic stress and forms the microtube depicted in Fig. 6. The length of the tube is $>200 \mu\text{m}$ and the diameter amounts to $4 \mu\text{m}$. About 80% of the length of the tube is completely detached from the substrate. Future work will concentrate on transferring this technology to much smaller tubes. The fabrication of capacitors will also

require an insulating film separating the p^{++} bilayer and the Cr film. The growth of multiple bilayers potentially permits the fabrication of dense arrays of tubes. Finally it has to be pointed out that this technology may also be used for the fabrication of biosensors as well as microfluidic and micromechanic devices.

3.2 Quantum cascade structures

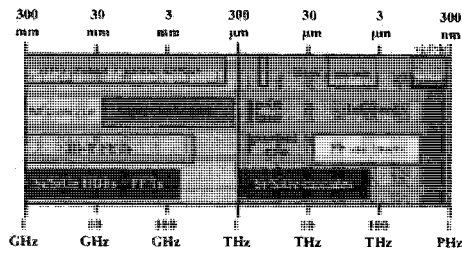


Figure 7. Illustration of the working frequencies of semiconductor devices unravelling the THz gap. SiGe QC lasers would have the potential to fill this gap (figure courtesy of D. Paul).

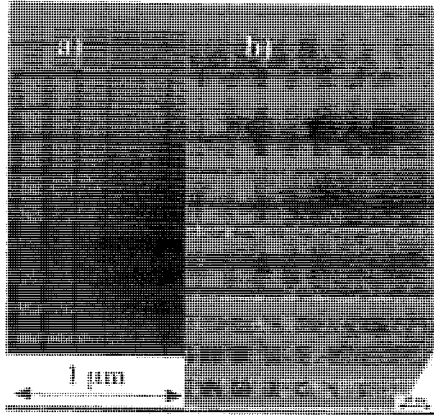


Figure 8. TEM micrograph of 30 period QC structure grown by MBE at 300°C, a) overview and b) 5 cascades at the bottom of the structure.

Even though quite intense photoluminescence has been observed in Si based nanostructures and optical gain has been reported for Si clusters embedded in an SiO_2 matrix [26], the goal to achieve strong electroluminescence, i.e. fabricating a Si based laser, has been out of reach so far for concepts based on interband transitions. Quantum cascade (QC) laser structures, which were first demonstrated using III/V quantum wells [27], appear to be a powerful alternative also for Si. Si/SiGe quantum cascade lasers have the potential to fill the so called THz-gap for wavelengths ranging from 20 to 100 μm as illustrated in Fig. 7. Big portions of the THz regime are not accessible for III/V devices, due to the strong interaction with phonons. But, strong absorption lines of many molecules in the THz regime allow for interesting applications in medicine, biology and chemistry, besides the potential of Si based opto-electronic devices for communication technology.

First results on pseudomorphic Si/SiGe QC structures were promising and electroluminescence

was observed in the mid-IR regime [28]. To expand the design freedom, increase the number of cascades and to incorporate a waveguide the concept was transferred to strain compensated $\text{Si/Si}_{0.2}\text{Ge}_{0.8}$ QC structures grown on relaxed $\text{Si}_{0.5}\text{Ge}_{0.5}$ buffer layers [29]. Following the bound to continuum design [30] structures with up to 30 periods were deposited using MBE at 300°C and a rate of 0.25 $\text{\AA/s}$. The design

using a chirped superlattice with increasing Si barrier width and a simultaneous decrease of the SiGe well width within the cascade, shifts the HH ground state from well to well to higher in energy. At a bias voltage of 70 kV/cm these states will line up and the minibands are formed. Note that only ground states are involved in this design. A cross sectional view taken by TEM of a structure containing 30 cascades, each containing 28 individual layers ranging in width from 0.4 to 2.8 nm is depicted in Fig. 8. These TEM micrographs indicate that there is no structural degradation through the whole stack of layers. The interfaces in the top cascades are as perfect as at the bottom of the structure. Extended studies using x-ray diffractometry and x-ray reflectivity give evidence that the QC structures are strain compensated towards the $\text{Si}_{0.5}\text{Ge}_{0.5}$ relaxed buffer layer, having an excellent reproducibility within the structure and from sample to sample and have abrupt interfaces.

Fig. 9 depicts a electroluminescence spectrum of the sample containing

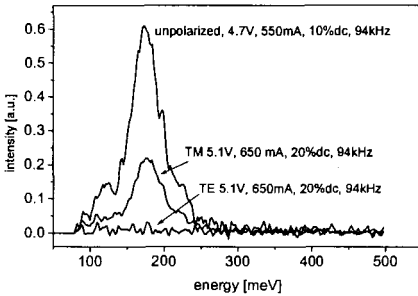


Figure 9. Electroluminescence spectra of a 15 period SiGe QC structures.

15 cascades. A pronounced peak is observed at 176 meV, which agrees well to the 156 meV expected from the design of the sample. The full width at half maximum amounts to 46 meV. The linewidth can be explained by interface roughness, since the Si barriers are very thin in the active region, down to only 0.4 nm and the wave function extend over several SiGe quantum wells. In addition also the non-parabolicity of the heavy hole states cannot be

neglected and will contribute to the linewidth. A more detailed discussion of the electroluminescence of these QC structures also in context with the VI characteristics can be found in ref. [29].

4 Conclusion

SiGe nanotechnology offers several viable paths for industrial applications in evolving future markets. It has the potential to cover the needs of mainstream microelectronic as well as niche market applications. Three subjects with interesting future perspectives have been discussed in detail. The Dot-FET may provide the advantages of high mobility n- and p-type channels without the use of problematic relaxed SiGe buffer layers with their low heat conductivity and high defect density. It is envisioned that self-scrolling of 3-dimensional nanoshells may relax space constraints on microchips by a compact fabrication of capacitors and coils, but may also enter into other fields like micromechanics and biotechnology. Finally, Si/SiGe quantum cascade structures might be suitable to fabricate a Si based laser.

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INVITED

SPIN RESOLVED INVERSE PHOTOEMISSION FROM LAYERED MAGNETIC NANOSTRUCTURES

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We report on the use of spin polarized electron beams in the study of electronic states in solids, referring in particular to the Inverse Photoemission spectroscopy. In this technique the empty electron states are investigated, and the spin resolution allows to study their spin character, yielding valuable information in magnetic systems. Examples of application to layered magnetic nanostructures are given: in particular we present data on Fe/Cr/Fe(001) multilayers, ultrathin Fe films grown on ZnSe(001), and LaSrMnO/SnTiO junctions.

1 Introduction

The ability of preparing thin metal films has recently generated a great deal of interest in their structural, electronic and magnetic properties, which may be radically different from their bulk counterparts. From a technological point of view, the understanding of such phenomena is promising for applications, as in the case of high-density magneto-optical storage media or of devices based on spin dependent transport properties. A crucial role in determining the magnetic properties of such 2-dimensional and related structures (multilayers) is played by the electronic states that are localized at the surface or at the interface between different layers. In magnetic systems these states may be efficiently probed by means of spin-polarized electron spectroscopies, thanks to the possibility of a direct identification of their spin character offered by spin resolution. In classical $3d$ ferromagnets there are less unoccupied than occupied d bands, resulting in less overlapping states in the empty region of the spectrum. It is then experimentally simpler to picture out the dispersion relation of the exchange split minority and majority bands, making the study of empty states in ferromagnetic structures particularly appealing. This task can be accomplished by means of spin resolved Inverse Photoemission (IPE): in this spectroscopy spin-polarized electrons are sent onto a solid surface while detecting the photons emitted in the radiative transitions towards the unoccupied states to be probed. The first spin-resolved IPE studies on bulk ferromagnets date back to the early eighties [1].

In the last decade, our group has contributed to this research field with a number of experiments on empty states. In our laboratory, in fact, a spin resolved IPE apparatus has been set-up by coupling standard ultra high vacuum (UHV)

techniques to an appositely designed spin resolved electron gun and high efficiency band pass photon detector [2]. The systems allows clean surface preparation and ultrathin film deposition via Molecular Beam Epitaxy (MBE), surface characterization via Low Energy Electron Diffraction (LEED) and X-ray photoemission Spectroscopy (XPS), and *in situ* IPE measurements. As usual in electron spectroscopies, measurements are performed in magnetic remanence (no applied magnetic field) with the sample magnetized along a crystal easy axis (*e.g.*, the [100] direction in case of Fe). The polarization of the electron beam, produced by a negative affinity GaAs photocathode, can be switched from parallel to antiparallel with respect to the sample magnetization. IPE spectra are collected in the isochromat mode, *i.e.*, by varying the beam energy and detecting only photons of a fixed energy (in our case $h\nu = 9.4$ eV), among the ones emitted in the electron decay towards the empty states (for details on the experimental apparatus, see Refs. [2]).

Different low dimensionality magnetic systems have been investigated, including surfaces, adsorbates, thin films, interfaces and multilayers. In the following we present an application of spin resolved IPE technique to study layered magnetic nanostructures, namely Fe/Cr/Fe(001) multilayers, Fe/ZnSe(001) ultrathin films, and LaSrMnO/SnTiO interfaces.

2 Fe/Cr/Fe(001) multilayers

Magnetic transition metals separated by thin non-magnetic layers exhibit an exchange coupling, with a ferromagnetic (FM) or antiferromagnetic (AF) character. In particular, Fe/Cr/Fe(001) multilayers have attracted considerable theoretical [3] and experimental [4,5] efforts. For this system an oscillating FM to AF coupling between the two Fe layers occurs, depending upon the thickness of the Cr spacer. Theoretical predictions, considering an ideal system with abrupt interfaces, sketch a magnetization profile in which the alignment of successive Fe layers can be figured out in terms of the trend towards AF coupling between adjacent layers within the Cr film and, at the same time, AF coupling between Cr and Fe atoms at the interfaces. This determines a FM (AF) coupling between Fe layers separated by an odd (even) number of layers of the Cr film. Experimental results state an opposite relation between the even or odd number of Cr layers and the Fe magnetic coupling: such a discrepancy is probably due to the formation of a mixed Cr-Fe phase at the interface which delays the onset of FM-AF oscillation [5]. The occupied electronic states of Cr/Fe systems have been investigated by several groups, also using spin resolved techniques [4,5]. We present here the study of the empty portion of the band structure above the Fermi level (E_F) by means of spin resolved IPE. In particular, we focus on films with a relatively large thickness (>7 monolayer, ML; 1 ML = 1.43 Å), while results on the early stages of the Cr/Fe(001) interface formation and ultrathin films can be found elsewhere [6].

A set of data for different Fe/Cr/Fe(001) trilayers are presented in Fig. 1. The left hand side of the Figure shows a sketch of the investigated samples, consisting of a clean Fe(001) substrate on top of which Cr and Fe films were deposited at room temperature at typical rates of 0.5-1.5 Å/min. The data discussed here were taken on trilayers with different values of the Cr spacer thickness, whereas the top Fe overlayer was in any case 7 ML thick.

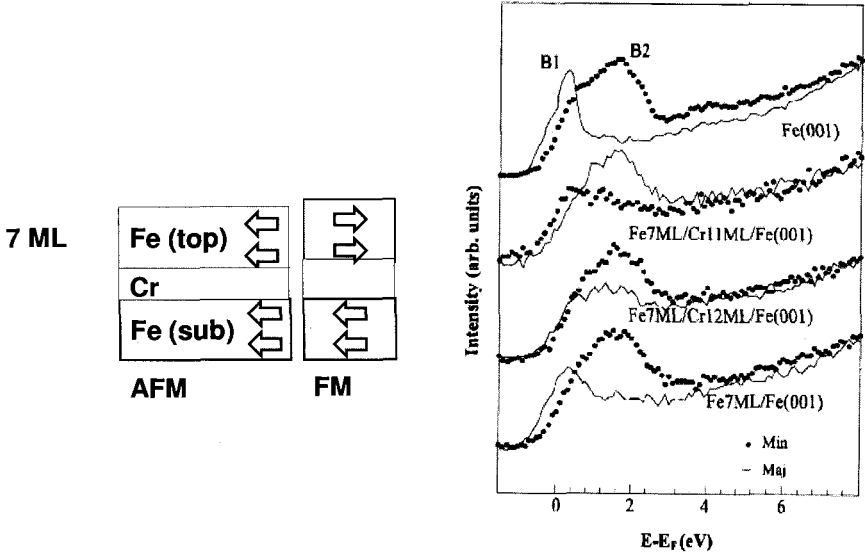


Figure 1. Spin resolved IPE spectra taken from clean Fe(001) and Fe/Cr/Fe(001) trilayers with an 11 ML and 12 ML thick Cr spacer. In the IPE spectra the majority- (continuous lines) or minority-spin (dotted lines) character is referred to the Fe substrate. The structure of the sample is also sketched.

The right hand side presents spin resolved IPE spectra for the Fe/Cr11ML/Fe(001) and the Fe/Cr12ML/Fe(001) systems, as well as those from the clean Fe(001) substrate, for a direct comparison. The coincidence of both short and long periods of the FM-AF transition when increasing the Cr spacer thickness from 11 to 12 ML [5], makes these systems very well suited to observe the switching of the magnetic coupling between Fe layers. In the spectra of Fig. 1, continuous (dotted) lines refer to data obtained for parallel (antiparallel) spin alignment between the incoming electrons and the majority electrons inside the Fe substrate. Thus, the structures B1 and B2 appearing in different spin channels of the Fe(001) spectrum have to be attributed to transitions towards majority- and minority-spin states, respectively, and constitute a clear evidence of the sample magnetic ordering [7]. In the case of the Fe/Cr/Fe trilayer spectra, we note first that the Fe overlayer is thick enough (7 ML) to hinder any sizable contribution from the underlying Cr film. The present measurements can then be interpreted in terms of pure Fe contribution, while the only role of the Cr spacer is to mediate the exchange interaction with the

substrate. Moreover, the reduction of the B1 peak intensity in the IPE spectra from the trilayer samples with respect to the clean substrate indicates a progressive decrease of the surface order when increasing the overall film thickness [2,7]. By looking at the polarization dependence, an AF coupling in the 11 Cr ML case is clearly seen: the spin character of the features present in the IPE spectra is indeed interchanged with respect to the clean surface. In the 12 Cr ML case, the spectra display the same spin character as the clean surface, indicating that now the magnetization of the Fe overlayer is in the same direction as the substrate below. This is a direct spectroscopic evidence of the switching from AF to FM coupling between the topmost Fe film and the buried Fe substrate when adding a single layer to the spacer, *i.e.* increasing the Cr film thickness from 11 to 12 ML.

3 Fe/ZnSe(001) ultrathin films

The control of the electron spin in semiconductors adds one degree of freedom, resulting in a very intriguing problem which holds potentials for the realisation of a new class of electronic devices with enhanced or completely new performances. In these systems attempts are done for controlling the carrier spin rather than its charge, adding the *spin-up spin-down* magnetic dualism to the conventional *electron hole* dualism, ruling all semiconductor devices. Spin electronics, nowadays commonly dubbed *spintronics*, is a fascinating and emerging field whose scientific and technological relevance is continuously increasing, that combines small scale (nanometric) magnetic elements with conventional semiconductor electronics [8]. In principle a convenient way to inject a spin polarized current into a semiconductor is based on the use of ferromagnetic metals like Co or Fe, fabricating hybrid ferromagnetic/semiconductor heterostructures. However a fundamental problem to be faced is the reactivity of transition metals with semiconductors, which can lead to magnetically dead layers, and in turn suppress the spin polarization across the interface. In this frame, interfaces fabricated on ZnSe substrates appear to be quite promising, offering more interesting properties than those based on more widely employed semiconductors, such as GaAs. At variance with the Fe/GaAs heterojunctions [8], in fact, recent studies on Fe/ZnSe(001) have shown that such interface is magnetically sharp, with Fe magnetic moment similar or even larger than bulk [9,10]. Furthermore the magnetic properties are stable up to 300 °C and the magnetism seem to be preserved in ultrathin films (coverages of the order of 1 ML), both results being important for device applications. We have prepared a clean ZnSe(001) substrate by UHV annealing of a ZnSe(001) epilayer grown on GaAs and passivated with a Se overlayer. Depending on the annealing temperature (300 to 420 °C), an (1x1) or a c(2x2) Zn rich surface reconstruction was obtained, as revealed by the LEED pattern, while XPS analysis indicated a clean surface with the correct Zn and Se stoichiometry. Despite the different initial conditions, we do not find any influence of the surface reconstruction in our IPE data. Ultrathin Fe layers

have been then deposited at a rate of about 0.5 ML/minute, with the sample kept at 170 °C, *i.e.* the optimal temperature for good epitaxial growth [10].

Fig. 2 presents a stack of IPE spectra taken at different Fe coverage, along with the reference spectra corresponding to the substrate (continuous line) and to a clean and well ordered Fe(001) surface (top spectra). The features A and D in the spectrum from clean ZnSe can be assigned to transitions between bulk states, as they display a sizable angular dispersion, typical of band-like states. The semiconductor behaviour is clearly evident from the delayed onset of the spectrum with respect to the Fermi level, E_F . The onset corresponds to the semiconductor conduction band minimum (CB), which, as estimated from the graphic extrapolation shown in Fig. 2,

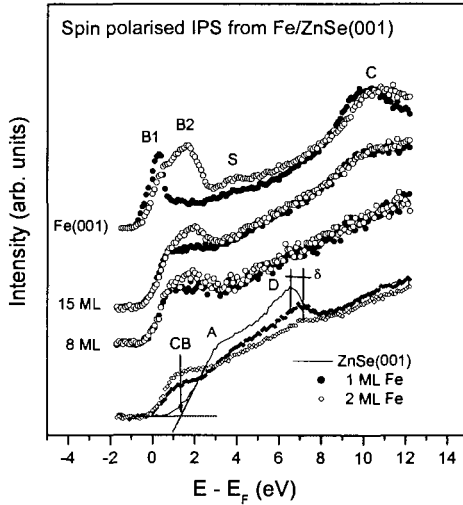


Figure 2. Spin resolved IPE spectra taken from Fe(001), Fe/ZnSe(001), and ZnSe(001).

is located around 1.3 eV above E_F . After deposition of 1ML of Fe new states appear at E_F , reflecting a metallic behaviour, while the features A and D shift towards higher energies. This shift ($\delta \sim 0.6$ eV) is related to the band bending induced by the Schottky barrier formation upon metal deposition. At 2 ML coverage the states at E_F , arising from Fe, grow up while A and D are attenuated. The energy position of these features does not change (within 0.1 eV) with respect to the situation of 1 ML. This indicates that the Schottky barrier height is stable upon further Fe deposition. The spectra referring to 1 and 2 Fe ML are spin integrated: no trace of spin polarization is seen up to 6-8 ML coverage, both at room temperature and at 100K. At 8 ML a difference between the spin-up and spin-down channels clearly appears at ~ 2 eV above E_F , in the region of the peak B2 of the pure Fe surface. As noted above, the absence of B1 is a common feature of a poor quality Fe surface [2,7], and indicates a non perfect layer by layer growth. The situation at 15 Fe ML is more or

less the same, even if there is a trace of B1 and we can observe the appearance of the peak C.

The present results show that the magnetic properties of ultrathin Fe films on ZnSe are quite different from those of bulk, in a completely similar way as in GaAs based interfaces. In particular, it is shown that spin injection into the semiconductor is possible only by using Fe films thicker than 8 ML. This will have strong impact on devices applications.

4 $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3$ interfaces

The search for 100% spin-polarized materials is a vital research area for spin electronics. In this sense manganites seem very promising systems, and in particular in the case of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO), a quasi half-metallic behavior at low temperature has been recently observed [11,12]. Despite these encouraging results, the electronic structure of this oxide is still not well known. Especially for the unoccupied density of states there is no experimental confirmation of theoretical calculations which predict a gap for the minority states. We present here an analysis of the electronic states of LSMO just above the Fermi level at different temperatures. The films were grown by Pulsed Laser Deposition (PLD) on a SrTiO_3 (STO) substrate [13,14]. In some cases they were covered by a STO layer. As the sample had been grown in a separate PLD system and then transferred in the electron spectroscopies apparatus, X-ray Photoemission Spectroscopy revealed the presence of some carbon and oxygen at the surface. Due to the difficulties inherent to any method for cleaning the surface of a complex oxide without alteration of the surface stoichiometry, measurements have been performed onto the sample as received. As a matter of fact this seems not so critical, since we succeeded in detecting the expected high spin polarization of LSMO through the contamination layer.

In Fig. 3a normal incidence IPE spectra from a free LSMO surface, taken at 100K and 300K are reported in the region near E_F . LSMO is a ferromagnet with a Curie temperature (T_c) around 350 K: however, on the basis the small value of the surface magnetization at 300K [12,13], we consider the room temperature spectra as representative of the non-magnetic insulating behavior above T_c . In fact, at 300K, there is no trace of spin polarization and the spin-integrated spectrum (bottom spectrum in Fig.3a) clearly displays the presence of a gap extending ~ 1 eV above E_F . The transition towards a low temperature half-metallic state is evident from the spectra taken at 100K (top-spectra in Fig. 3a), where two distinct line-shapes for the majority- (full dots) and minority-spin channels (empty dots) are visible. The sample appears metallic for majority electrons and insulating for minority electrons, as it results from the delayed onset of the spin down channel. Due to the very low counting rate at E_F and to the effect of the rescaling procedure to 100% polarization of the incident electron beam, data present a sizeable scattering. This prevents from a precise determination of the spin polarization at E_F , which is however definitely

above 90%. On the other hand the delayed onset of the minority channel is clearly visible, and can be related to the onset of the t_{2g} minority band. The position of the low energy edge of this band with respect to E_F can be estimated from the energy difference δ between the minority and majority-channel onset: we find $\delta = 400 \pm 50$ meV.

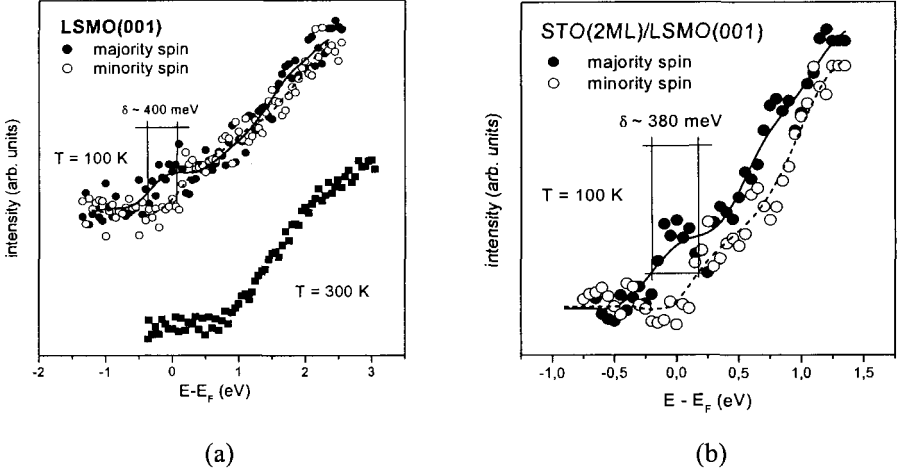


Figure 3. (a): Spin integrated IPE spectrum from LMSO taken at 300K (squares in the bottom) and spin resolved data (full and empty dots on top) taken at 100K. (b): Spin resolved IPE spectra taken at 100K from a LSMO film covered by two monolayers of STO. A smoothing of experimental data at 100K is plotted for the two spin channels: majority spin – continuous line, minority spin – dashed line.

The results for the STO/LSMO interface at 100K, where the sample is ferromagnetic, are reported in Fig. 3b. The sample consists of 2 ML of STO grown on LSMO(001) in the typical conditions employed for tunneling junctions [11,13]. Also in this case we find a delayed onset of the minority spin electrons and a value for δ which is very close to that previously found for the free surface: 380 ± 50 meV. Our findings then clearly indicate that the LSMO half-metallicity is preserved also when a STO/LSMO interface is created, in agreement with the very high value of the tunneling magnetic resistance observed in similar junctions [11,13].

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INVITED

NONLINEAR OPTICAL PROPERTIES OF ONE-DIMENSIONAL PHOTONIC CRYSTALS

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An overview of nonlinear interactions in finite, one-dimensional, photonic band gap structures with deep gratings is presented. Second harmonic generation and optical limiting are considered in detail. Some quantum aspects of nonlinear propagation and noise reductions are also discussed.

1 Introduction

For more than half century semiconductors have had a prominent role to play in almost every field of technology thanks to the ability to tailor their conductive properties. Just as tailoring the properties of semiconductors constituted a challenge several decades ago in solid state physics, today tailoring the properties of photonic crystals (PC) may hold the key to achieving significant technological advances in the field of photonics. For this purpose we believe that a new class of materials, called photonic band gap (PBG) structures, appears to hold much promise. One-dimensional (1-d) PBG structures are made by arranging macroscopic dielectric and/or metallic unit cells into a periodic or quasi-periodic array, in order to affect the properties of the light in almost the same way that semiconductor crystals affect the properties of electrons. The periodic arrangement results in allowed and forbidden frequency bands and gaps for the light, in analogy to energy bands and gaps of semiconductors.

The systematic study of PBG materials began with the works of Yablonovitch [1] and John [2] on spontaneous emission control and light localization. These contributions gave a way to an intense theoretical and experimental investigation of PBG structures that has continued since. Some of the applications that have been proposed over the years include photonic crystals fibers [3], photonic crystals circuits [4], transparent metal-dielectric stacks [5], highly efficient micron-sized

devices for nonlinear frequency conversion [6-13]. An up to date review of recent advancements in the field of PBG structures may be found in reference [10].

2 Quadratic nonlinear interaction

The scalar nonlinear Helmholtz equations governing the quadratic interactions of two linearly polarized plane waves at fundamental frequency (FF) ω , and SH frequency 2ω in a layered, 1-D, finite structure can be written as [11 – 15]:

$$\frac{d^2 E_\omega}{dz^2} + \frac{\omega^2 \varepsilon_\omega(z)}{c^2} E_\omega = -2 \frac{\omega^2}{c^2} d^{(2)}(z) E_\omega^* E_{2\omega}, \quad (1a)$$

$$\frac{d^2 E_{2\omega}}{dz^2} + \frac{4\omega^2 \varepsilon_{2\omega}(z)}{c^2} E_{2\omega} = -4 \frac{\omega^2}{c^2} d^{(2)}(z) E_\omega^2, \quad (1b)$$

where $\varepsilon_{j\omega}(z)$ ($j=1,2$) are the spatially dependent, linear dielectric functions for the FF and SH fields. In general, $\varepsilon_{j\omega}(z)$ are assumed to be complex functions. The condition $\varepsilon_\omega(z) \neq \varepsilon_{2\omega}(z)$ takes into account possible material dispersion. Finally, $d^{(2)}(z)$ is the spatially dependent quadratic coupling function.

In spite of their apparent simplicity, Eqs. (1) admit no known, general analytical solutions. Eqs. (1) can be integrated numerically by resorting to a nonlinear matrix transfer technique [15], assuming no pump depletion and a weak nonlinearity. The analysis of Eqs. (1) can be simplified considerably by identifying two different spatial scales of variation of the electric fields: (i) a fast-scale, which accounts for oscillations that may occur within a spatial scale on the order of the wavelength due to linear interference effects; and (ii) a slow-scale, which takes into account the nonlinear polarization source terms on the right-hand side of Eqs. (1): the role of the nonlinearity is to modulate the linear solution over a length scale much longer with respect to the fast scale. In order to separate fast and slow-scale variations we introduce a new set of independent variables, $z_\alpha = \lambda^\alpha z$ with $\alpha=0,1,2,\dots$, where λ is a dimensionless parameter. Once the multiple scales expansion [14] has been performed, the procedure calls for the application of the limit $\lambda \rightarrow 1$ to restore the original space variable z . Under this hypothesis, the system of equation governing the nonlinear interaction can be written in a very simple form starting from the following representation

$$E_{j\omega}^{(1)} = A_{j\omega}^{(+)}(z_1, z_2, \dots) \Phi_{j\omega}^{(+)}(z_0) + A_{j\omega}^{(-)}(z_1, z_2, \dots) \Phi_{j\omega}^{(-)}(z_0) \quad (2)$$

where $\{\Phi_{j\omega}^{(\pm)}\}$ are the left-to-right (LTR) and right-to-left (RTL) linear modes that are functions of fast variable z_0 . LTR and RTL modes can be calculated using a standard linear matrix transfer technique, assuming a unitary electric field is incident on the structure from LTR for the $\Phi_{j\omega}^{(+)}$ modes, and from RTL for the $\Phi_{j\omega}^{(-)}$ modes. We note that $\Phi_{j\omega}^{(\pm)}$ carry information about the linear localization properties

of electric field inside the structure, and $A_{j\omega}^{(\pm)}(z_1, z_2, \dots)$ are the complex amplitudes of the fields that depend on the slow variables $z_1, z_2, \dots$:

$$\sum_{l=+,-} p_{\omega}^{(+,l)} \frac{dA_{\omega}^{(l)}}{dz} = i \frac{\omega}{c} \sum_{(k,l)=(+,-)} \Gamma_{(\omega,+)}^{(k,l)} A_{2\omega}^{(k)} A_{\omega}^{(l)*}, \quad (3a)$$

$$\sum_{l=+,-} p_{\omega}^{(-,l)} \frac{dA_{\omega}^{(l)}}{dz} = i \frac{\omega}{c} \sum_{(k,l)=(+,-)} \Gamma_{(\omega,-)}^{(k,l)} A_{2\omega}^{(k)} A_{\omega}^{(l)*}, \quad (3b)$$

$$\sum_{l=+,-} p_{2\omega}^{(+,l)} \frac{dA_{2\omega}^{(l)}}{dz} = i \frac{\omega}{c} \sum_{(k,l)=(+,-)} \Gamma_{(2\omega,+)}^{(k,l)} A_{\omega}^{(k)} A_{\omega}^{(l)}, \quad (3c)$$

$$\sum_{l=+,-} p_{2\omega}^{(-,l)} \frac{dA_{2\omega}^{(l)}}{dz} = i \frac{\omega}{c} \sum_{(k,l)=(+,-)} \Gamma_{(2\omega,-)}^{(k,l)} A_{\omega}^{(k)} A_{\omega}^{(l)}, \quad (3d)$$

where $p_{j\omega}^{(k,l)} = \left\langle \Phi_{j\omega}^{(k)} \left| \hat{p}_{j\omega} \Phi_{j\omega}^{(l)} \right\rangle\right.$, for $j=1,2$ and $k,l=+,-$,

$$\Gamma_{(\omega,n)}^{(k,l)} = \left\langle \Phi_{\omega}^{(n)} \left| d^{(2)} \Phi_{2\omega}^{(k)} \Phi_{\omega}^{(l)*} \right\rangle\right., \quad \Gamma_{(2\omega,n)}^{(k,l)} = \left\langle \Phi_{2\omega}^{(n)} \left| d^{(2)} \Phi_{\omega}^{(k)} \Phi_{\omega}^{(l)} \right\rangle\right..$$

The overlap coefficients $\Gamma_{(j\omega,n)}^{(k,l)}$ are effective, complex coupling coefficients that reflect the way in which the LTR and RTL modes sample the distribution of the nonlinearity $d^{(2)}(z)$ over the structure. The values of $\Gamma_{(j\omega,n)}^{(k,l)}$ are maximized, and can be greater than the magnitude of $d^{(2)}(z)$, when the fields interact coherently inside the structure. Since no assumptions were made regarding the type of grating, Eqs. (3) are valid for arbitrary index profiles and tuning conditions. We note that this formulation allows analytical solutions in the undepleted pump regime [14]. We also note that Eqs. (3) are valid when the steady state regime is approached.

For the second harmonic generation, we find that above a certain input intensity a dynamics reminiscent of a competitive, multi-wave mixing process occurs: the pump field is mostly reflected, revealing a novel type of optical limiting behavior, while forward and backward generation is generally balanced. We also study the case of parametric down-conversion, where an intense second harmonic signal is injected in order to control a much weaker fundamental beam. Our results reveal the onset of a new process that has no counterpart in bulk materials: both transmission and reflection display an unexpected, unusual, resonance-like effect as functions of input second harmonic power.

3 Optical limiting with photonic crystals

Other interesting applications of nonlinear behavior of a one-dimensional metallo-dielectric photonic band gap (PBG) structure concern with the optical limiting

properties. When two photon absorption is present, the nonlinear transmission dependence on the incident light intensity has been found, mainly due to the light confinement in the structure which enhances the nonlinear response of the materials. Specifically, we studied a four period sample where the single period consists of ZnO and Ag layers respectively 109 and 17 nm thick. The structure was designed so to exhibit a transmission resonance at 532 nm. Under Q-switched frequency doubled Nd:YAG laser, a transmission decrease of the order of 50% has been found for a maximum incident light intensity of 2 GW/cm^2 . The obtained results are explained in terms of the change of the absorption coefficient due to two photon absorption and show that the structure is suitable for the realization of optical limiting devices [16].

The third order nonlinearity in the dielectric structure allows a route to new concepts of optical limiting, taking into account transverse instabilities [17].

4 Noise reduction during in a parametric process

Quadrature–amplitude and phase squeezing are investigated in planar waveguide geometry under conditions for which the use of a linear grating fabricated on top of the waveguide reproduces a photonic band gap structure. The introduction of a nonlinear grating, obtained with a modulation of the nonlinear susceptibility $\chi^{(2)}$, provides an additional degree of freedom, that allows, together with the linear grating, to tune the fundamental field in a selected resonance of the transmission spectrum and, at the same time, to control the phase-matching condition between the fundamental and second harmonic field. The results show that quadrature-phase squeezing is achieved for the fundamental field, increasing the second-harmonic input intensity. The second harmonic field is tuned in the pass band of the PBG. The low nonlinear conversion efficiency, given by a suitable selection of the mismatch, gives rise to the possibility of having a fundamental field of quite the same intensity, but less noisy than at the entry. The PBG structure of the waveguide provides a reduction of the dimension of the device [18].

5 Conclusion

Many interesting phenomena and results can be found studying nonlinear optical properties of one-dimensional photonic crystals. The availability of strong light confinement and tailoring of the dispersive properties allows to design and develop new miniaturized devices for photonic circuitry.

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TUNABLE THREE-DIMENSIONAL PHOTONIC CRYSTALS BASED ON OPAL-VO₂ COMPOSITES

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Three-dimensional opal-VO₂ based photonic crystals were prepared by the chemical bath deposition technique. The x-ray diffraction and Raman spectroscopy confirm the crystalline perfection of VO₂ impregnated into synthetic opal pores. It is shown from the optical reflectivity measurements that the photonic bandgap of the opal-VO₂ based photonic crystals composite is governed by the phase transition in VO₂. The shift of Bragg diffraction spectra under the pulsed (10 ns) illumination of YAG:Nd laser has been also observed in the opal-VO₂ composites.

1 Introduction

Photonic crystals are materials, whose dielectric constant is modulated with a period comparable with the light wavelength [1]. The Bragg diffraction of light in such a periodic structure gives rise to a photonic band gap (PBG) in the spectrum of electromagnetic eigenstates of the crystal. This means that the light propagation in the spectral range coinciding in the energy with the PBG will be suppressed in a certain direction (a stop band) or in all directions (a complete PBG). Current interest in photonic crystals is primarily due to their perspective applications to control light propagation, to create thresholdless microlasers and all-optical transistors, and to increase the coherency time of states in quantum computers.

A good example of a three-dimensional photonic crystal is synthetic opal [2], having a fcc lattice composed of close-packed monodisperse amorphous SiO₂ spheres with a diameter varying within 100–1000 nm. The PBG position may be tuned in a wide spectral range (UV–near IR) by varying the size of SiO₂ spheres.

Many potential applications require a use of special methods to control the PBG structure of a material in real time under external effects (electric field, strain, heating, etc.). To create the 3D PBG material tunable in real time it was suggested [3-5] infiltrating the opal pores with liquid crystal (LC). This approach allows tuning the characteristics of a PBG structure owing to an electro-optic effect in the LC, when an electric field is applied. However, the long response time of LCs restricts their application to the millisecond range. Transition to shorter times involves the search for materials, whose dielectric constant can be changed by an external effect in the nano-, pico-, and femtosecond ranges.

For this reason, a perspective alternative may be a photonic crystal based on opal–vanadium dioxide (VO_2) composite, with a semiconductor - metal phase transition in VO_2 . Experiments on pump–probe measurements of the VO_2 phase transition, which use pulses from mode-locked lasers, have shown that this transition occurs for a period of several hundreds of femtoseconds [6].

2 Samples preparation

In this work, we synthesized original opal – VO_2 composites. The initial templates used were commercial synthetic opals with a polydomain structure. The size of a domain with a high ordering degree of SiO_2 spheres was 30–100 μm . The experimental samples were 5×5×0.1 mm plates cut parallel to the (111) opal plane. The diameter of the SiO_2 spheres was 230 ± 5 nm. The opal pores were initially filled with V_2O_5 by the chemical bath deposition technique. The V_2O_5 was reduced to VO_2 by annealing in air at 800°C and constant total pressure of 0.1 Torr [7].

3 Samples characterization

The composite structural perfection was studied by XRD and Raman spectroscopy. The x-ray data presented in Fig. 1(a) show that the composite does not contain other vanadium oxides except VO_2 .

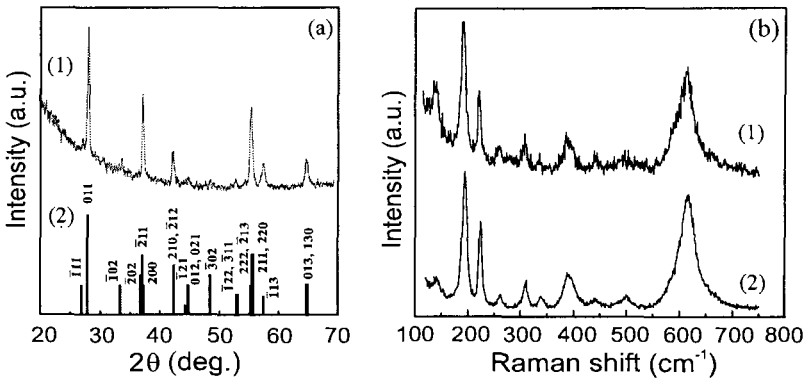


Figure 1. (a): X-ray diffraction patterns of (1) the opal- VO_2 composite and (2) the bulk monoclinic VO_2 sample. (b): Raman spectra of (1) the opal- VO_2 composite where VO_2 is in the semiconductor phase and (2) the single VO_2 crystal [7].

Fig. 1(b) illustrates the Raman spectra from the reference sample (a VO_2 single crystal) and the opal- VO_2 composite, where VO_2 is in the semiconductor phase. Analysis of the spectra has shown that the frequencies and full width at half maximum of the phonon lines registered in the composite spectrum are in a good agreement with those for the single VO_2 crystal.

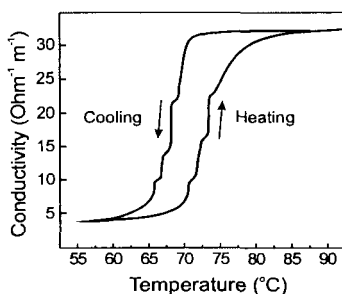


Figure 2. Thermal hysteresis loop of the opal-VO₂ composite conductivity [7].

The results on the temperature dependence of conductivity of the composite in the vicinity of the semiconductor-metal phase transition testify to the crystalline perfection of VO₂. Fig. 2 shows the thermal hysteresis loop of the composite conductivity, measured at direct current in the temperature range of 20–90°C. Of interest are the following features of the experimental curves. First, the heating branch begins at the temperature of 67°C, coinciding with that for single crystal VO₂. This indicates the stoichiometry of VO₂ in synthesized samples. Second, the hysteresis loop has a practically symmetrical shape, i.e., the heating and cooling branches of the loop are parallel. This is evidence of a low concentration of oxygen defects.

4 Inverted opal - VO₂ composites

The inverted VO₂ photonic crystal was formed on the basis of opal template. In the first stage, voids of the opal template were preliminarily filled with a solution of V₂O₅ in nitric acid and then V₂O₅ was reduced to VO₂ through the high-temperature annealing of a sample in vacuum. In the second stage, the composite was subjected to inversion by etching out the skeleton of SiO₂ spheres with HF acid [8, 9].

As shown by SEM studies, the thus-synthesized samples were entirely composed of VO₂ and had the form of an inverted replica of the opal template, reproducing spatially its fcc structure (Fig. 3). The difference between the inverted sample and the starting opal consists in that intersphere voids of the opal are filled with crystalline VO₂ and SiO₂ spheres are removed. The former places of the spheres are now occupied by air voids surrounded by a skeleton of crystalline VO₂.

The aforesaid is confirmed by an electron micrograph of the surface of a synthesized sample. The image shows a (111) section of the outer layer of spherical voids, with a lattice of white regions corresponding to the section of the VO₂ skeleton; the gray regions inside this lattice represent the whole set of lower

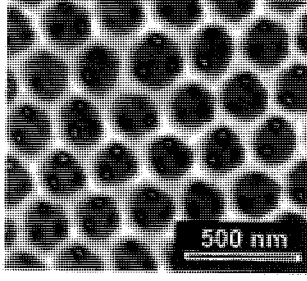


Figure 3. SEM image of a vanadium dioxide photonic crystal with inverted opal structure [10].

half - spheres of the cut-off layer. Moreover, dark apertures are well seen in each half-sphere at the places of sintering between SiO_2 spheres in the opal template. These apertures connect the spherical voids.

5 PBG properties of opal - VO_2 based composites

To study the PBG properties of synthesized composites, we measured the specular reflection spectra from the (111) lattice planes of opal- VO_2 . To avoid any contribution of the opal polydomain structure and structural defects to the signal being measured, we used the so-called light microscopic technique [9]. It allowed investigation of a fragment of the sample surface within a single domain. To study the phase transition effect on the PBG properties, the samples were heated by a resistance microheater.

Fig. 4(a) presents the reflection spectra from the (111) composite surface at normal light incidence. The spectra were measured at two temperature values: below the phase transition temperature (the semiconductor phase) and above it (the metallic phase). The observable peaks are due to the Bragg diffraction of electromagnetic waves by the periodic structure of the samples, characterizing the stop band in the [111] direction.

The spectral position of the Bragg peak at normal incidence is defined by the relation

$$\lambda_m = 2d_{111}\sqrt{\langle\epsilon\rangle}$$

where d_{111} is the interplane distance in the fcc lattice of the composite in the [111] direction, $\langle\epsilon\rangle$ is the average dielectric constant of the composite; $\langle\epsilon\rangle = \sum \epsilon_i f_i$, where ϵ_i and f_i are the dielectric constant and the volume fraction of the i-th component of the composite, respectively.

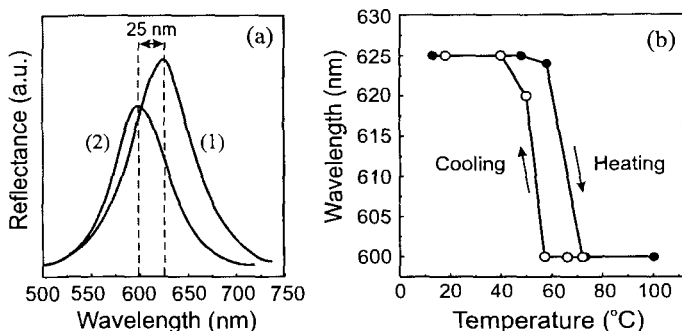


Figure 4. (a) Reflection spectra from the (111) surface of the opal-VO₂ composite: 1 - VO₂ in the semiconductor phase, T=15°C; 2 - VO₂ in the metallic phase, T=75°C. (b) The thermal hysteresis loop of the reflection peak position for the (111) surface of the opal-VO₂ composite during the sample heating and cooling [7].

The sample heating leads to the phase transition in VO₂, changes its dielectric constant, and decreases the average dielectric constant and the optical contrast. As a result, the Bragg diffraction peak shifts towards the shortwave region by about 25 nm. Fig. 4(b) shows the thermal hysteresis loop of the Bragg peak position. The loop configuration and the temperature range coincide with the electric measurements presented in Fig. 2. Note that a good reproducibility of all spectral characteristics was observed in numerous heating-cooling cycles.

Fig. 5 shows experimental specular-reflection spectra for a domain of the inverted VO₂ photonic crystal synthesized in this study. It can be seen that the reflection peak, corresponding to PBG, is shifted by 38 nm upon the semiconductor-metal phase transition to shorter wavelengths. Fig. 5(b) presents temperature hysteresis loops of the peak position in the reflection spectra of an inverted composite (VO₂ photonic crystal).

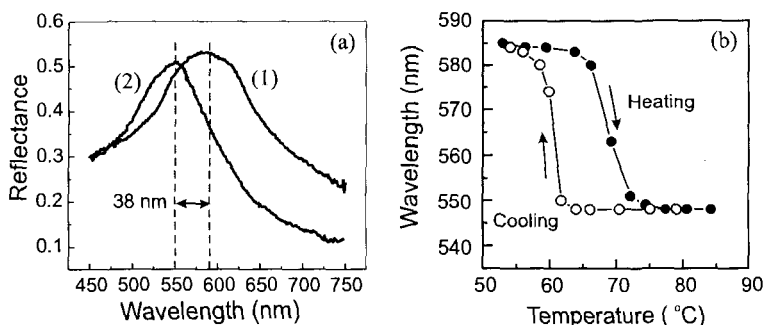


Figure 5. Reflection spectra from the (111) surface of the inverted VO₂ photonic crystal (a): 1 - VO₂ in the semiconductor phase, T=15°C; 2 - VO₂ in the metallic phase, T=87°C. (b) The thermal hysteresis loop of the reflection peak position for the (111) surface of the opal-VO₂ composite during the sample heating and cooling [10].

Quantitative calculations of the reflection spectra were carried out using the transmission matrix method. The best agreement between theory and experiment is achieved at $\epsilon'=7.5$, $\epsilon''=0.48$ (where ϵ' and ϵ'' are real and imaginary parts of VO_2 dielectric constant, correspondingly) for the semiconductor phase and $\epsilon'=6.1$, $\epsilon''=0.36$ for the metallic phase [10].

6 Laser pulses induced Bragg switching

We have also realized dynamical switching of PBG position under pulse optical heating [11]. In our experiments the sample was excited at room temperature by 10-ns pulses of second harmonic of YAG:Nd laser ($\lambda=530$ nm, repetition rate of 1 kHz). The power density P_l applied to the sample was varied from 0.5 up to 6 mJ/cm². The measured signals $\Delta I(t; \lambda)/I_0(\lambda)$, where $I_0(\lambda)$ is the stationary intensity of reflected light at fixed wavelength, are shown in Fig. 6(a). The signal measured at $\lambda_1 > \lambda_m$ is negative, while the signal measured at $\lambda_2 < \lambda_m$ is positive (λ_1 and λ_2 are shown by arrows in the inset of Fig. 6(a)). This result confirms that observed signal is due to a spectral shift of Bragg diffraction spectra under the laser pulses. The signals measured at different P_l at λ_2 are shown in Fig. 6(b). It is seen that all signals have a sharp leading edge and long decay with a 10–100 μs mean time constant. The amplitude and duration of the signals depend on P_l .

The energy of light quantum of laser pulse exceeds the band gap of VO_2 . Thus, optical pulses are strongly absorbed by VO_2 and free carriers are created. After the fast relaxation of photoexcited carriers, the local temperature T of the optically excited volume near the sample surface increases. If P_l exceeds some threshold, the value of T becomes higher than T_c during the laser pulse and we observe dynamical blue shift of Bragg diffraction spectra due to the phase transition in VO_2 . In the ideal homogeneous case, when the changes in temperature $T(t)$ and phase transition take place synchronously in the whole excited volume, we should observe rectangular signal (dashed line in Fig. 6(a)). It should have a sharp leading edge when T becomes higher than T_c , a constant part while T decreases to T_c and a fast decay when T becomes lower than T_c . The amplitude of $\Delta I(t, \lambda)$ should be equal to the difference between signals in stationary spectra and the duration should correspond to the cooling time from $T > T_c$ to T_c .

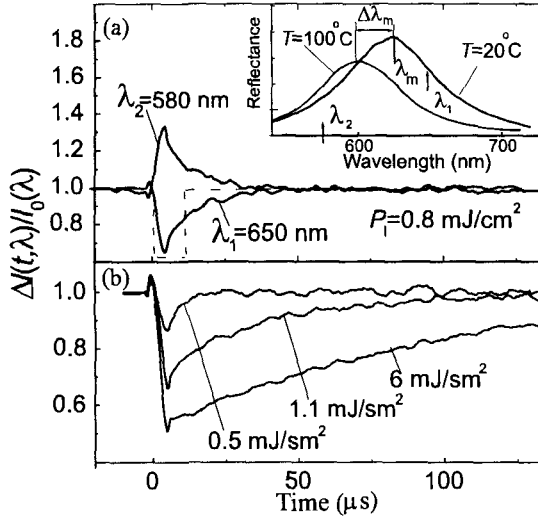


Figure 6. (a) Dynamical signals $\Delta I(t, \lambda)/I_0(\lambda)$ induced by laser pulses measured at different λ . The inset shows the stationary reflection spectra from (111)opal plane at $T < T_c$ and $T > T_c$; (b) Dynamical signals $\Delta I(t, \lambda)/I_0(\lambda)$ measured at $\lambda_2=650$ nm at different P_1 . The dashed line shows the expected signal in the case of homogeneous heating and cooling processes [11].

Thus we should expect the increase of the pulse duration with the increase of P_1 . This increase is actually observed experimentally (Fig. 6(b)). However, the shape of the measured pulse is not rectangular. We explain the shape of $\Delta I(t, \lambda)$ by the non-uniform heating of VO₂ during laser pulses and the further cooling process. The reasons for this are the small penetration depth of light into the sample and the inhomogeneous thermoconductivity properties of opal-VO₂ polydomain composite.

7 Conclusion

To conclude, we have synthesized VO₂ with a perfect crystal structure in opal pores using the chemical bath deposition technique. The parameters of the semiconductor–metal phase transition in the prepared material indicate the presence of a small amount of oxygen defects. We have achieved a controllable and reproducible variation of the PBG properties of the opal-VO₂ composite and inverted VO₂ composite during heating and cooling. This is due to the change in the dielectric constant of VO₂ at the phase transition. We demonstrated dynamical tuning of the PBG position in synthetic opals filled with VO₂ under laser pulses.

The above results combined with experiments on the effect of femtosecond-scale laser pulses on the optical constants of crystalline VO₂ films [10], give one grounds to assume that the Bragg spectrum switching at the application of ultrashort laser pulses in photonic opal-VO₂ crystals may occur in times less than 1 ps.

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INTERBAND TRANSITIONS IN SI NANOSTRUCTURES WITHIN EFFECTIVE MASS APPROXIMATION

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Electron and hole states have been calculated for Si nanowires and quantum dots within the effective mass approximation. In the calculation of the electron states, six anisotropic valleys of bulk Si have been taken into account. It is found that the states depend on the crystallographic direction and on the size of the wires and the dots. These results have been used to calculate electron-hole recombination lifetimes. The magnitudes of the lifetimes are very sensitive to the geometrical and structural parameters of the wires and the dots. It is concluded that non-uniformity in the crystallographic direction of Si nanowires and quantum dots causes itself dispersion in the values of the photoluminescence lifetime.

1 Introduction

The research of the properties of Si nanostructures has been promoted by recent progress in fabrication of low-dimensional semiconductors in the nanometric scale for applications in transistor and memory devices. The electrical properties of Si nanowires, nanopillars and arrays of dots are the subject of current research. Porous Si seems now promising for applications in the field of photonics and sensing including important perspectives in biosensing.

Porous Si consists of a network of crystalline silicon wires and/or dots in the nanometer range with dispersion of sizes and shapes. A lot of insights in physics and properties of porous Si [1-7] have been gained by the theoretical investigation of these systems. Moreover, other systems containing silicon quantum dots or nanowires have been investigated so as the intrinsic properties due to dots or wires have been demonstrated [8-12]. Empirical, semi-empirical and first principle techniques have been used to study theoretically the effects of the reduction in dimensions, of the geometry and the structure on optical properties of silicon nanostructures [13-28]. All the calculations found a widening of the band gap from the near-infrared wavelength region to and beyond the visible range. It has been shown that the confinement results in an enhancement of the dipole matrix element that is responsible for radiative transitions. Both direct and indirect band gaps have been reported. Most calculations are restricted to particular cases of geometries and sizes of the dots and wires. Continuous values can be used for structural parameters within effective mass approximation (EMA) and so further evidence of new physical mechanisms that can be directly connected with the experiment can be

obtained. The predictions of EMA for the energy band structure of electrons in Si nanowires have been discussed in detail in [29] where the findings of EMA are also compared with results of more sophisticated calculations. The implications of the features of the electron band structure on the spontaneous emission have been discussed in [30] and the behavior of the photoluminescence (PL) lifetime in Si quantum wires with dimensions in the range of a few nanometers has been discussed in [31].

In this paper, we present some of our results on Si nanowires and quantum dots. The PL lifetime is calculated as a function of the crystallographic direction and the size of the wires and the dots. We have considered sizes in the range of 1–4 nm and crystallographic directions varying in (100) plane from [100] to [110] direction. Here, we discuss representative results on wires and dots of size ~ 2 nm.

2 Model

We consider free standing, homogeneous wires and dots. The wires have a rectangular cross section and are infinitely long. The dots are cubes. Electron and hole eigenstates are obtained by solving Schrödinger equation for each ellipsoid valley of bulk Si conduction band minimum. An infinitely deep confining potential is assumed. We define a system of coordinates (x,y,z) as follows: the z axis is along the [001] direction and the x and y axes are rotated anticlockwise by an angle θ relative to the [100] and [010] directions, respectively. The quantum wire infinite length is along the y-axis. The quantum dots have finite length of the same size in all x,y,z directions.

In Si quantum wires, six valleys in the conduction band of Si are not equivalent and every set of valleys gives a sequence of two-dimensional energy subbands. The minima of these energy subbands are at the Γ -point (direct subbands) or away from the Γ -point (indirect subbands), depending on the wire orientation and origin of the valley. The position of the minimum in the ground subband determines direct or indirect bandgap character of the wire. The order and the separation of the energy subbands depend strongly on the confinement dimensions of the wires, i.e. L_x and L_z for a wire in the y-direction. Effective mass approximation predicts a strong dependence of the energy band structure on the confinement, via L_x and L_z , but also on their ratio L_x/L_z [29].

In Si quantum dots the anisotropy of bulk Si valleys causes a deviation of the electron states from simple sinusoidal functions in the case of cubic dots. Schrödinger equation is solved numerically [32]. The six valleys of bulk Si give distinct levels. The order and the separation of the energy levels depend on the size and on the crystallographic direction of the dot.

In Si nanowires and quantum dots of a few nanometers the number of excited e-h pairs is small due to considerable confinement and our system consists of independent e-h pairs. Therefore, our discussion refers to a single e-h pair recombination. The lifetime, τ , is defined as the inverse of the recombination rate.

The expressions for direct and for phonon assisted recombination of a single e-h pair are given in [31] for the quantum wires and in [32] for the quantum dots.

3 Results and discussion

3.1 Si quantum wires

We consider recombination of a single e-h pair. The hole occupies the ground subband. The electron energy levels versus the wire direction for a quantum wire with confinement dimensions $L_x=2.0$ nm, and $L_z=2.2$ nm are shown in Fig. 1. It can be seen that for an electron, the separation between the ground subband and the first subband depends on the wire orientation and for certain directions it can be very small [29,30]. There are two distinct types of subbands. *I subband* originates from the valley in the [100] direction and its minimum moves away from the Γ -point (when $\theta=0$ deg) as the orientation of the quantum wire changes from [100] to [110]. *D subband* originates from the valley in the [001] direction and its minimum is at the Γ -point for all directions of the quantum wire.

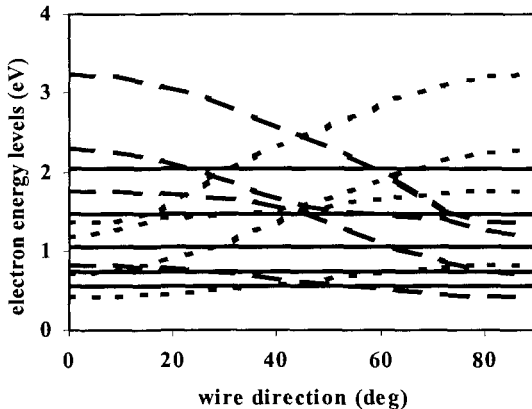


Figure 1. Electron energy levels versus wire orientation for a quantum wire with confinement dimensions $L_x=2.0$ nm and $L_z=2.2$ nm. Electron states are shown from the three pairs of valleys in [001] (solid lines), [010] (dashed lines) and [100] (dotted lines) directions. Energy levels are expressed relative to the bottom of the bulk Si conduction band.

The calculated PL lifetimes at room temperature for the two subbands as a function of the wire orientation are presented in Fig. 2. The lifetime for the D subband does not depend on the wire orientation and it is of the order of μsec . Its magnitude depends on the overlap integral that is well smaller than unity in the case of Si wires. The overlap integral is determined by the confinement dimensions and the phase of the wavefunction. The phase of the wavefunction is given analytically within EMA and it is related with the bulk properties of Si and with the wire orientation [31]. The lifetime for the I subband shows a strong directional dependence, that is due to the directional dependence of the energy band structure through the overlap integral. I subband is a direct one for $\theta=0^\circ$, and an indirect for

$\theta \neq 0^\circ$. Now, for $\theta = 10^\circ$, the minimum of the I subband is not very far from the Γ -point and so direct transitions are possible. These transitions become less probable as θ increases and this is why the PL lifetime increases as it is shown in Fig. 2 by the dotted line. At bigger angles, recombination is due to indirect transitions and the magnitude of lifetime depends on the wire orientation in the same way as in the low temperature regime.

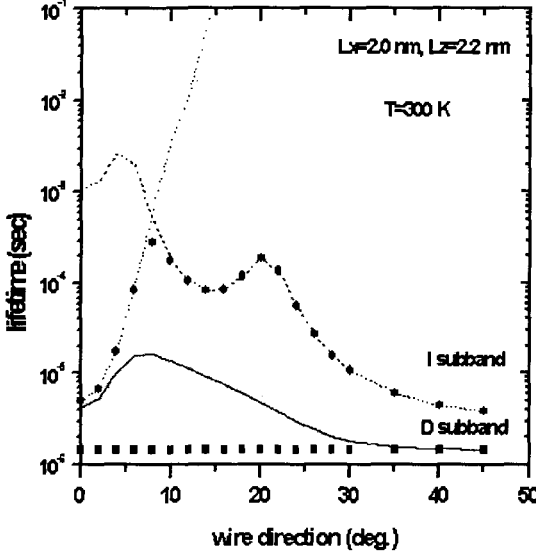


Figure 2. The calculated PL lifetime as a function of the wire orientation, at room temperature, for the I subband (dots) and for the D subband (squares). The dashed line is for the direct transitions of the I-subband and the dotted line is for the phonon-assisted transitions of the I-subband. The solid line is for the total PL lifetime of the quantum wire.

The above distinct features of the PL lifetimes when electrons occupy the I subband or the D subband show that the lifetime strongly depends on the electronic structure of the quantum wire. Thermal activation from one subband to the other is also important as it is shown in the following analysis. At low temperatures, only the ground subband is occupied and the dependence of the lifetime on the wire direction is shown in Fig. 1 by a solid line. At room temperature, occupation of the first excited subband may be activated and the resulting lifetime is then given by the following expression:

$$\tau^{-1} = \frac{\tau_F^{-1} e^{-\Delta E/kT} + \tau_S^{-1}}{1 + e^{-\Delta E/kT}},$$

where τ stands for the total PL lifetime and $\Delta E = E_F - E_S$ for the energy separation of the two subbands. The subscripts F and S are for 'fast' and 'slow' subbands respectively, and refer to the D subband or the I subband, depending on which is faster or slower than the other. The total lifetime calculated at room temperature is presented in Fig. 2, together with the lifetimes for the I and D subbands by a solid line. For angles $0^\circ < \theta \leq 10^\circ$, the lifetime is that of I subband, because although this is

the ‘slow’ subband, it has big energy separation from the D subband (the ‘fast’ subband) in comparison with the thermal energy. For angles $10^\circ < \theta \leq 30^\circ$, the energy separation between the ‘slow’ I subband and the ‘fast’ D subband is comparable with the thermal energy and the lifetime time is determined by Boltzmann statistics for the occupation of the two electron subbands. For $30^\circ < \theta \leq 45^\circ$, the lifetime is that of the D subband because it is the ‘fast’ subband and the ground subband. It can be noticed in Fig. 2 that the lifetime shows a variation of one order of magnitude at room temperature as the wire orientation changes from [100] to [010].

For a quantum wire with the same size but the inverse ratio of confinement dimensions, i.e. $L_x=2.2$ nm and $L_z=2.0$ nm and ratio $\lambda=L_z/L_x=0.9$, the ground subband is D subband for all wire orientations [29,30] and the PL spectrum as well as the PL lifetime are not sensitive to the wire orientation.

3.2 Si quantum dots

We consider recombination of a single e-h pair. The hole occupies the ground subband. In Fig. 3, we show the lowest energy electron levels that originates from the [001] valley (dots) and [100] valley (squares) versus the dot crystallographic orientation for the dimension $L=2.0$ nm. It can be seen that for an electron, the separation between the two levels depends on the dot orientation.

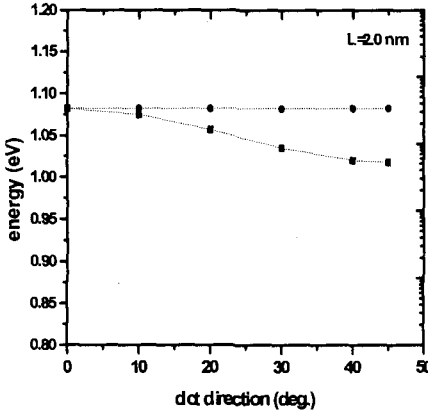


Figure 3. Electron energy levels versus dot direction for a cubic dot of with width $L=2.0$ nm. They are shown the first electron state from the valley [001] (dots) and the first electron state from the valley [100] (squares). Energy levels are expressed relative to the bottom of the bulk Si conduction band.

The calculated PL lifetimes for the two levels as a function of the dot orientation at room temperature are presented in Fig. 4. The lifetime for the [001] valley level does not depend on the dot orientation. First order and second order transitions dominate depending on the dot orientation. The magnitude of the lifetime depends on the confinement dimensions and phase of the wavefunction that for the dots as for the wires is given analytically within EMA [32]. The electron that

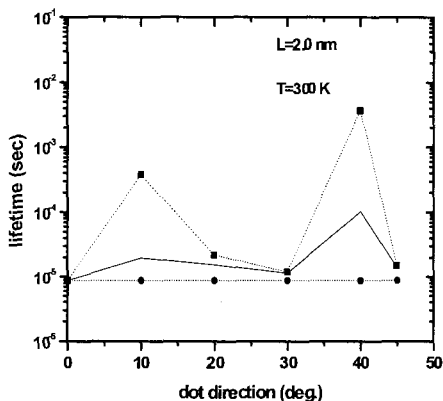


Figure 4. The calculated PL lifetime as a function of the dot direction, at room temperature, for the states described in Fig. 3. The dotted lines are guides to the eye. The solid line is for the total PL lifetime of the quantum dot.

occupies the ground energy level can be excited to a higher level and recombine from there. The resulting lifetime is shown in Fig. 4 by solid line. It shows dispersion in magnitude depending on the dot orientation.

4 Conclusion

It has been shown that interband transitions in Si nanostructures can be described within effective mass approximation and their interesting behavior has been found. It has been shown that in Si nanostructures the separation between the energy levels is not determined solely by the confinement dimension but also by the crystallographic direction due to the character of the anisotropic valleys of bulk Si conduction band minimum. Recombination from electron states originating from different valleys can have quite different lifetimes. The energy separation between states originating from different valleys differs depending on the size and orientation of the wires and the dots. Electrons can be thermally excited from the ground to an excited level and recombine from there with a smaller PL lifetime. It can therefore be concluded that non-uniformity in the size and/or in the crystallographic orientation of a network of nanowires and/or quantum dots cause dispersion in the PL lifetime.

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PHOTOLUMINESCENCE OF Er^{3+} IONS IN OPAL/TELLURITE GLASS COMPOSITE NANOSTRUCTURES

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Composite nanostructures consisting of an opal matrix containing tellurite glass doped with Er^{3+} ions have been synthesized and photoluminescence of Er^{3+} embedded in these structures in comparison with tellurite glass has been examined. A noticeable enhancement of luminescence in opal matrix as compared to glass has been observed. Possible enhancement mechanisms are discussed.

1 Introduction

Three-dimensional nanostructures with a characteristic period on the order of electron de Broglie wavelength or optical photons wavelength are considered as promising and challenging for a number of applications in nanoelectronics and nanophotonics [1]. Electron and photon confinement effects inherent in these structures result in controllable light emission and propagation including modification of emission spectra, transition probabilities, spatial and polarization characteristics of emitted radiation [1-3]. A synthetic route based on self-organization of nanocomponents in a three-dimensional periodic lattice is probably the most appropriate approach to fabrication of large-scale three-dimensional lattices with a submicrometer period. Silica colloidal crystals known as natural or artificial opals whose iridescence arises from multiple interference in a 3-dimensional dielectric lattice of spherical globules represent such a type of structures [3]. Opals and opal-based three-dimensional structures are considered as prototypes for design and investigation of photonic crystals exhibiting photonic bands within the visible and near-infrared spectral range. Such structures are shown to be promising for novel lasers and optical amplifiers [4, 5]. In this case, doping of opal-based matrices with erbium is of crucial importance since erbium is the main optoelectronic component providing optical gain in the operation range of modern optical communication industry.

In this contribution, we perform synthesis and primary studies of opal/glass nanostructures containing Er^{3+} ions and established an enhanced luminescence as compared to a reference glass sample on a fused silica substrate.

2 Results and discussion

Opal matrices have been fabricated using monodisperse silica sol as a precursor by means of a prolonged sedimentation and subsequent hydrothermal heat treatment. Globule diameter was 250 nm. A typical electron-microscope image of an opal surface indicating a periodic three-dimensional lattice is presented in Fig. 1. Fabrication of samples based on opals and reference glass samples have been performed in identical conditions as were the conditions of the samples testing. Structures based on tellurite glass have been obtained by means of radio-frequency (rf) magnetron sputtering of cold targets containing 70% of TeO_2 , 20% of WO_3 , 6% of La_2O_3 , and 4% of Er_2O_3 in an oxygen-argon atmosphere. Gas pressure was 0.2 Pa, rf-discharge density being 6 W/cm^2 with frequency 13.6 MHz. After deposition the structures were subjected to a heat treatment in air (30 min at 350 °C).

Photoluminescence spectra have been measured at room temperature using a semiconductor laser as an excitation light source ($10^3 \text{ W}/\text{cm}^2$ at 980 nm). Luminescence light has been collected by a lens condenser and then dispersed with a grating monochromator (MDR-23). Light detection was performed by a germanium photodiode DPD 2000 (Dilas Co.). A silicon filter was used to additionally cut off the excitation radiation.

Photoluminescence spectra of Er^{3+} ions in an opal-based matrix containing tellurite glass and in a reference glass sample deposited on a silica substrate are presented in Fig. 2. A considerable enhancement of emission in the opal-based matrix as compared to the reference sample is evident and indicative of the promising approach performed in this study for synthesis of efficient erbium based optoelectronic components.

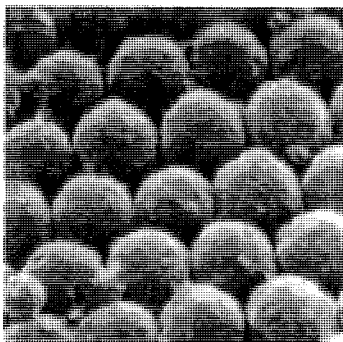


Figure 1. A fragment of an opal surface, $1 \times 1 \mu\text{m}^2$.

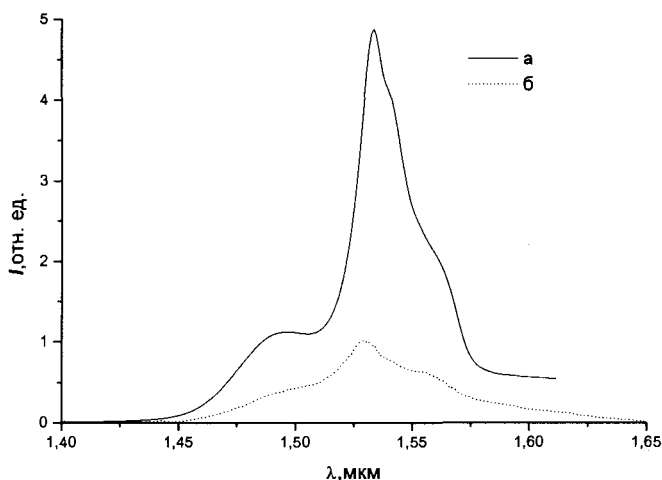


Figure 2. Erbium photoluminescence in an opal/glass matrix (a) and in a plain glass sample (b).

Two factors are to be discussed as possible reasons of the luminescence enhancement in opals as compared to a plane structure [9,10]. First, a significant increase in the internal surface and multiple scattering of exciting radiation in such samples may result in more efficient absorption of excitation light because of a small photon mean free path in an opal matrix. Second, spectral and angular redistribution of photon density of states may alter radiation rate and angular distribution of emitted light. The mechanisms of luminescence enhancement will be examined in more detail in the forthcoming research.

3 Conclusion

In conclusion, three-dimensional periodic nanostructures containing erbium ions have been fabricated based on artificial opal matrices. Their photoluminescence efficiency was found to be higher as compared to a reference glass sample. Possible reasons responsible for enhancement include enhanced excitation efficiency due to increase in efficient absorption length and modification of spontaneous decay of ions in a periodic lattice due to redistribution of photon density of states.

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TIME-RESOLVED LUMINESCENCE OF EUROPIUM COMPLEXES IN BULK AND NANOSTRUCTURED DIELECTRIC MEDIA

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Time-resolved luminescence of europium complexes with organic ligands is investigated in several nonpolar organic solvents, xerogel, porous glass, and opal-polymer photonic crystals. Possible explanations of nonexponential luminescence decays of Eu^{3+} ions in nanostructured dielectric environments are discussed.

1 Introduction

The idea of environmentally controllable spontaneous emission put forward in the 1940s by Purcell [1] has recently stimulated numerous experiments on spontaneous emission in various microheterogeneous environments such as microcavities, thin dielectric slabs, dielectric interfaces, and biological membranes. Investigations of spontaneous emission in photonic crystals (see, e.g., [2] and refs. therein) are of particular interest. In these investigations, various light-emitting species – organic molecules, semiconductor nanocrystals, and rare-earth ions – were used as spontaneously emitting probes. The success of such experiments of the type critically depends on the choice of the reference system and possibility to discriminate between contributions of different mechanisms of excited state deactivation.

Chelates of rare-earth ions are promising compounds for applications as probes of modified density of electromagnetic modes. However, the possibility of their

successful application depends on the stability of their photophysical properties upon embedding into nanostructured dielectric environments. Here, we report preliminary experimental data on luminescence kinetics of two europium chelates (tris(1,5-hexafluoro-2,4-pentanedionate) bis(trioctyl-phosphine oxide) europium (III) (Eu^{3+} -(HFAC)₃-(TOPO)₂) and tris(benzoyl trifluoroacetate) mono(4,7-diphenyl-1,10-phenanthroline) europium (III) (Eu^{3+} -(BTFA)₃-BPhen)) in organic solvents, solid polymer films, xerogel, porous glass, and opal-based photonic crystals.

2 Experimental

Eu^{3+} -(HFAC)₃-(TOPO)₂ [3] was kindly provided by Dr. G. L. J. A. Rikken (High Magnetic Fields Laboratory, CNRS, Grenoble), Eu^{3+} -(BTFA)₃-BPhen was synthesized according to an original protocol. Thin films of europium complexes in polystyrene were prepared by dissolving both compounds in chlorobenzene, followed by spin coating on quartz glass substrates. Artificial opals were produced from a highly monodisperse silica sol by prolonged sedimentation in an aqueous medium and subsequent hydrothermal annealing. Opal samples were characterized by scanning electron microscopy and optical transmission/reflection measurements. Opal-polymer photonic crystals were prepared by filling the sublattice of voids in opal with a solution of Eu chelate in prepolymerized styrene followed by slow polymerization. In a similar manner, Eu chelates were introduced in xerogel and porous glass samples.

Steady-state and time-resolved luminescence measurements were carried out at room temperature. A nitrogen laser was used as an excitation source in measurements of luminescence decays. Time-resolved luminescence spectrally selected at 613 ± 2 nm by a custom-made interference filter was detected using a FÉU-83 photomultiplier tube and digitized by an ADC computer board.

3 Results and discussion

Photophysical properties of organic chelates of europium ions are well known and extensively described in the literature. Eu chelates exhibit an intense absorption band at about 300–350 nm due to organic ligands and can be efficiently excited in this spectral range. Luminescence spectra of these compounds are dominated by the line at ~613 nm corresponding to the $^5D_0 \rightarrow ^7F_2$ electric dipole transition in Eu^{3+} ions. The large Stokes' shift is a considerable advantage of these compounds in the context of the present study, since it virtually eliminates the possibility of luminescence reabsorption in strongly scattering (micro)heterogeneous media such as photonic crystal structures. Due to shielding of the Eu^{3+} ion from the environment by organic ligands, in nonpolar media these complexes exhibit high

luminescence quantum yields and excited-state lifetimes in the submillisecond range, which substantially simplifies time-resolved luminescence experiments.

In nonpolar solvents, Eu chelates studied in the present work exhibited luminescence kinetics closely following the single exponential decay law over the intensity range of about three orders of magnitude. In agreement with the previous observations [5, 6], an increase in the refractive index of the nonpolar medium leads to a systematic decrease in the excited-state lifetime of the Eu ion. This effect is accounted for by the well-known refractive-index dependence of the radiative rate $k_{rad} = nf^2(n)k_{rad}^{vac}$, where k_{rad} and k_{rad}^{vac} are radiative rates in a dielectric medium and *in vacuo*, respectively, n is the refractive index of the medium, and $f(n)$ is the local-field correction factor [4, 5].

In solid environments, however, luminescence kinetics of the Eu chelates becomes nonexponential. To provide an adequate model-independent data analysis, distributions of decay times $F(\tau)$ were recovered from measured luminescence kinetics according to the formula $\int_{\tau_{min}}^{\tau_{max}} F(\tau) \exp(-t/\tau) d\tau = I(t)$, where $I(t)$ is the

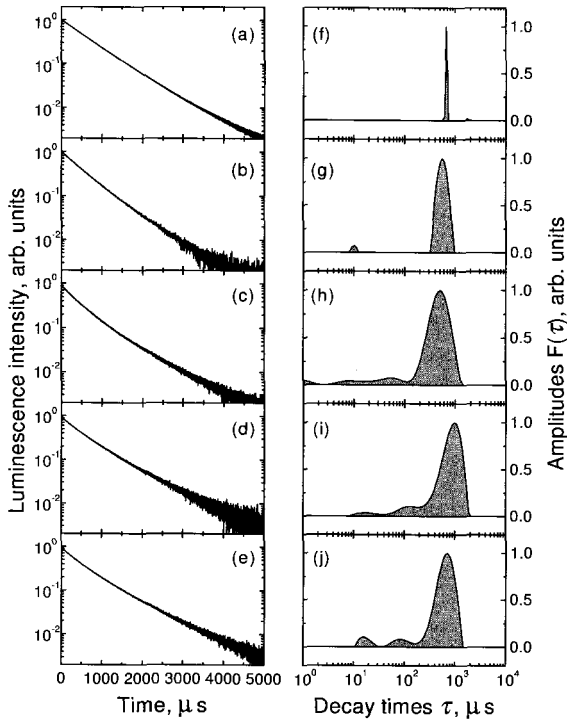


Figure 1. Luminescence kinetics (a–e) and corresponding decay time distributions (f–j) for $\text{Eu}^{3+}\text{-(BTFA)}_3\text{-BPhen}$ in toluene (a, f), polystyrene film (b, g), porous glass (c, h), xerogel (d, i), and opal-polymer photonic crystal (e, j).

luminescence intensity decay. Inversion of time-resolved data was carried out by a regularized method described in [6].

As it is evident from Fig. 1, the luminescence decay deviates from the single-exponential law in a homogeneous polymer film, Eu^{3+} . In nanostructured media, the nonexponential character of Eu^{3+} luminescence kinetics becomes more pronounced. This phenomenon can be explained by the joint effect of perturbation of the chelate structure upon embedding in the porous medium and changes in the local properties of the environment during the polymerization process, as well as by spatial distribution of local-field correction factors in the heterogeneous dielectric. In the case of the opal-based photonic crystal, an additional contribution to the dispersive intensity decay can be expected from the modified density of electromagnetic modes. Further detailed investigations are required to conclude on relative contributions of these effects to the observed nonexponential kinetics of Eu^{3+} luminescence in nanostructured dielectric media.

Acknowledgements

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SYNCHROTRON INVESTIGATIONS OF ELECTRON-ENERGY SPECTRA IN SILICON NANOSTRUCTURES

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With the use of synchrotron radiation X-ray near-absorption edge spectra in the range of Si $L_{2,3}$ -edges were obtained for the first time in the following objects: nanostructures with Ge quantum dots grown on Si substrates and porous Si layers obtained by anodic electrochemical etching of single-crystalline Si $\langle 100 \rangle$ and $\langle 111 \rangle$. These spectra represent (s+d) partial density of states in the conduction band. All nanostructures demonstrate quantum-size effects as an appearance of additional level at 2-3 eV from the bottom of the conduction band as well as dependence of the band gap in the investigated materials on these effects.

1 Introduction

Crystalline and amorphous materials containing nano-size clusters draw a serious attention due to their unique physical properties.

The purpose of this work is to investigate electron yield spectra of the samples containing nanometer-scale clusters and quantum dots applying synchrotron radiation. Electron yield spectra correspond to X-ray absorption near-edge spectra (XANES) and they allow to determine local partial density of states (LP DOS) with certain symmetry into unoccupied states of the conduction band of different materials.

2 Experimental

XANES investigations were made at Russian-German beamline of BESSY synchrotron radiation facility. Energy resolution was of 0.03 eV. Ultrasoft X-ray

emission spectra (USXES) were obtained with X-ray laboratory spectrometer-monochromator RSM-500. Energy resolution was 0.2 eV. The depth of analysis in both cases was about 10-20 nm.

Porous silicon was fabricated by a standard technique of electrochemical etching in the alcohol solutions of hydrofluoric acid at the different time of etching.

Growing of the epitaxial Er doped Si layers was performed by sublimation molecular-beam epitaxy method. Layers with Ge quantum dots were also grown by sublimation molecular-beam epitaxy method in GeH_4 .

3 Results and discussions

3.1 Porous silicon

XANES of por-Si grown on monocrystalline plates c-Si are presented in Fig. 1.

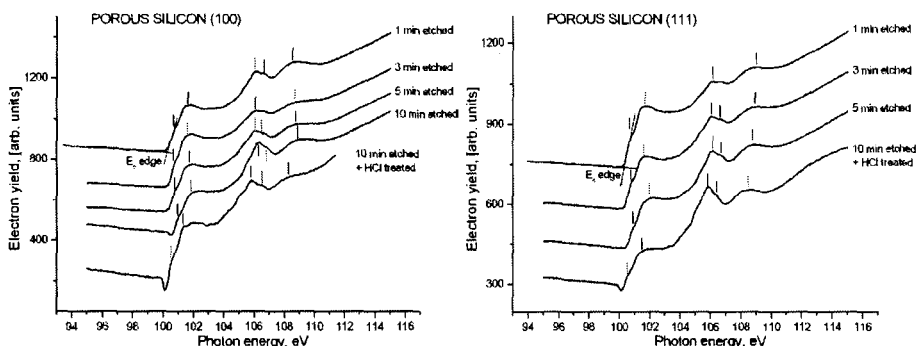


Figure 1. XANES spectra near Si $L_{2,3}$ absorption edge of porous silicon grown on c-Si substrate $\langle 100 \rangle$ - left and $\langle 111 \rangle$ - right with different etching time.

Energy features of electron yield spectra of por-Si grown on c-Si $\langle 111 \rangle$ and $\langle 100 \rangle$ practically are not distinguished. Comparing these results with reference spectra [1] that porous silicon consists of two main phases: amorphous silicon and silicon oxide.

After treating of porous silicon in a solution of HCl a noticeable reconstruction of XANES is observed (Fig. 1). For both types of the substrate orientation the slope of the spectra near absorption edge becomes more sharp. This effect is revealed especially for the sample on $\langle 100 \rangle$ oriented substrates as a considerable increase in relative intensity in the range of c-Si edge. It means that there is different kind of chemical activity relative to chemical reagents in the surface layers of porous silicon depending of the substrate orientation which [2].

Earlier, we had developed the method of phase composition determination for por-Si surface layers by Si $L_{2,3}$ USXES data by computer fitting of experimental Si $L_{2,3}$ -spectra with the model one [3]. According to the data obtained from USXES

there are more phases in porous layer: amorphous silicon, silicon oxide, crystalline silicon, low-coordinated Si [4] and sub-oxide ($\text{SiO}_{1.3}$). The latter phase, probably, can be regarded as a thin oxide film covering the surface of silicon nanocrystals. Therefore, results of two investigation methods, XANES and USXES, do not contradict but complete each other.

Thus, from the analysis of XANES and USXES data and SEM and AFM-images it follows that porous silicon is a multi-phase system containing nanocrystals of silicon covered with amorphous and oxide phases. Under laser excitation of visible photoluminescence electrons can transfer from conduction band bottom of the oxide phases to the valence band of silicon resulting in a broad luminescence band in the range of 1.8 - 2.4 eV.

3.2 Si-based nanostructures

Si L XANES of multilayer nanostructures, grown on c-Si $\langle 100 \rangle$ substrates are presented in Fig. 2. In this series we have investigate multilayer nanostructures of two groups. The first group samples contain Er doped epitaxial layers of Si obtained by sublimation molecular-beam epitaxy. The second group samples contain layers with Ge quantum dots which were produced by sublimation epitaxy in GeH_4 . All the investigated structures with quantum dots were capped by thin silicon layers of about 50 nm.

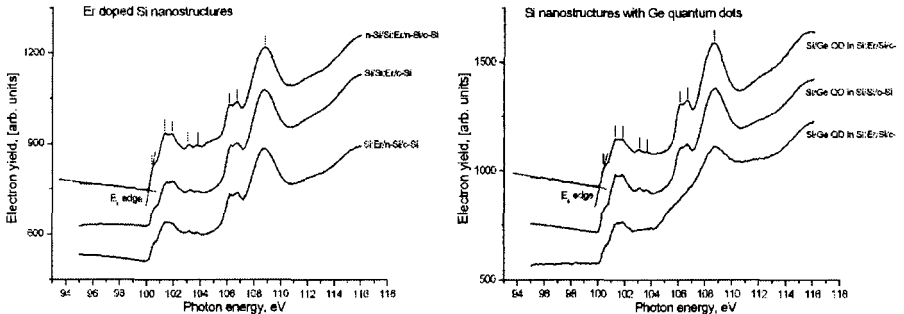


Figure 2. Si $L_{2,3}$ XANES of Si nanostructure with Er doped layers (left) and Si nanostructure with Ge quantum dots (right).

The spectra of samples with layers which contain strained silicon bonds - Ge/Si quantum dots and Si:Er - are characterized by the developed fine structure in the energy range of 101 - 104 eV. Nobody has ever observed such fine structure up to now. Corresponding energy levels in the conduction bands can participate in the luminescence spectra. The most striking thing here is a close similarity of the Ge/Si spectra and Si:Er samples. Nevertheless, one should remember that surfaces of practically all nanostructures were capped with thin protecting epitaxial layer of

~ 50 nm silicon. It means that the strain at the border of quantum dots passes through the cap layer.

We also note that most of both series samples are more or less oxidized. That is proved by the presence of XANES peaks in the range of 106.2 - 108.8 eV, which correspond to silicon-oxygen chemical bonds.

4 Conclusion

- XANES and USXES data were used to determine phase composition of surface layers and energy level diagram in porous silicon. Porous silicon consists of Si microcrystals covered with amorphous silicon and silicon oxides.
- A model of photoluminescence in por-Si on the basis of XANES and USXES data allows to explain its appearance due to electron transitions from the oxide levels to silicon ones. A set of energy levels determined by XANES and USXES spectra of corresponding phases assumes existing of optical transitions in the range of 1.8 - 2.4 eV, characterizing photoluminescence of por-Si.
- XANES Si L_{2,3}-spectra were obtained for the first time in Ge/Si quantum dots and in Si:Er-based structures. Just nanocrystalline silicon structures demonstrate distinguished additional peaks in these spectra (about 102 - 103 eV). Corresponding energy levels in the conduction bands can participate in the visible luminescence.

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STRAIN-INDUCED PHOTOLUMINESCENCE RED SHIFT OF InGaAs /GaAs MICROTUBES

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Photoluminescence (PL) of individual microtubes containing GaAs quantum wells has been examined by means of microfluorescence spectroscopy. PL spectrum of a microtube was found to exhibit a pronounced red shift by about 70 meV with respect to the reference planar film. The shift is attributed to an interplay of strain effects on semiconductor band structure.

1 Introduction

A strain in semiconductor layers modifies their band structure. Proper choice of the strain distribution enables changing optoelectronic properties of semiconductor structures which is valuable for application. An approach to three-dimensional (3D) micro- and nanostructuring using built-in strains in pseudomorphically grown semiconductor heterostructures proposed recently [1] allows to create free-standing objects of various shapes [2,3]. After detaching from a substrate, initially flat strained heterofilm bends owing to elastic relaxation of mechanical stress and forms a free-standing object. Strain distribution in the final 3D object differs from that in the initial flat film which results in difference in optical properties [4]. In the present work, we study photoluminescence (PL) spectrum of an InGaAs/GaAs microtube containing an biaxially strained GaAs quantum well (QW).

2 Results and discussion

The structure was grown by molecular beam epitaxy (MBE) on a GaAs (100)-oriented substrate and contained, above a GaAs buffer layer, an AlAs sacrificial layer (10 nm), an $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$ strained layer (18.5 nm), an $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ lower barrier (12 nm), a GaAs QW (10 nm), an $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ upper barrier (20 nm) and a GaAs cap layer (12 nm). By means of optical lithography and wet etching stripe-shaped mesastructures were defined on the initial sample. The longest sides of the mesastructures were oriented in $\langle 010 \rangle$ direction in order to obtain long tubes without ruptures (see the anisotropy of Young's modulus in III-V compounds [5]).

Fig. 1 shows a formation scheme and a tube obtained. The elastic forces F_1 and F_2 give rise to a moment M of forces which tends to bend the bilayer. The initial structure consists of AlAs sacrificial layer, InGaAs compressed layer and a complex layer with i-GaAs quantum well and AlGaAs doped barrier. The tubes were rolled up by means of selective etching of an AlAs sacrificial layer with HF-based etchant [6]. The diameter of the tubes was about 10 micrometers.

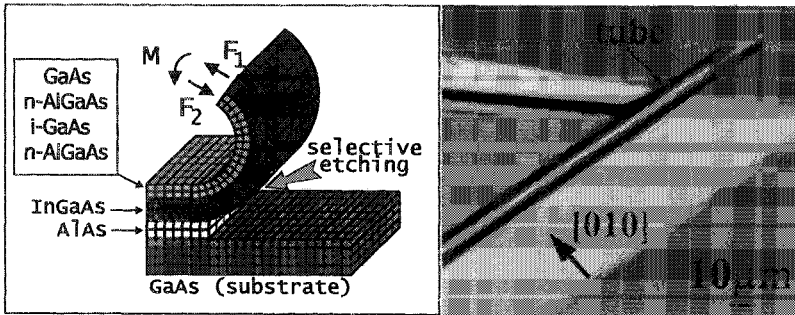


Figure 1. Left: Schematic view of the self-scrolling process. Right: Photograph of a fabricated tube.

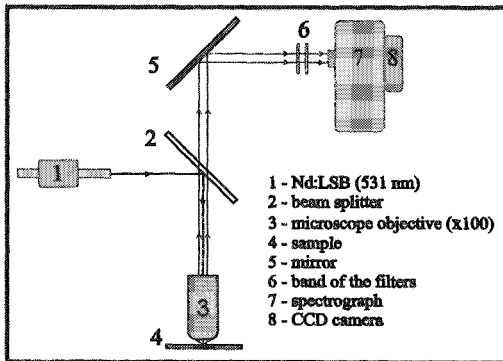


Figure 2. Experimental setup for local PL spectra measurements.

PL measurements were performed using high-sensitive micro-photoluminescence setup consisting of a microscope, an imaging grating spectrograph (Solar TII, Minsk) and a liquid nitrogen cooled CCD-camera (1200×300 pixels, Princeton Instruments). Image of the sample surface under investigation was transferred to the entrance slit of the spectrograph, then distersed and examined with the CCD detector (Fig. 2). Solid state cw-Nd-laser (Nd-LSB, LEMT, Minsk) provided excitation radiation at the wavelength 531 nm with an average power at the sample surface about 10^2 W/cm^2 . Measurements were taken at room temperature.

Fig. 3 shows PL emission spectra of initial heterofilm and the heterofilm detached from substrate and rolled-up in a tube. After rolling the PL peak of QW is shifted toward lower energy by about 70 meV (from 1.50 eV to 1.43 eV). The reason of the red shift is redistribution of strains in the heterofilm after rolling. Initially unstrained GaAs QW after releasing is under tensile strain due to the balance of moments [7,8]. The tensile strain reduces the band gap of QW, which results in the observed red shift of the PL emission spectra. The quantitative estimates of the strain effects on band gap shift [9] in the structures investigated are in a good agreement with the observed data and will be described in more detail elsewhere.

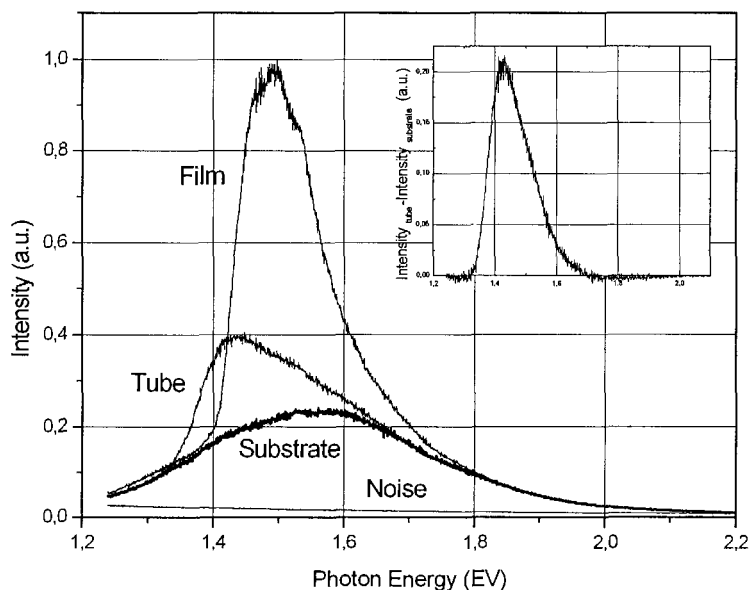


Figure 3. Photoluminescence spectra of the plane film, the microtube, and the substrate.

3 Conclusion

In conclusion, we perform microphotoluminescence studies of a microtube containing InGaAs quantum well and evaluated a pronounced red shift of PL emission spectra of a microtube as compared to a reference plane film. The shift is well described by the biaxial strain effects. The structures investigated are rather interesting in the context of polarization of PL emission modified in microtubes as compared to planar structures. These will be the subject of the forthcoming paper.

Acknowledgement

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EFFECTS OF DOPING AND NONRADIATIVE DEFECTS IN GaAs SUPERLATTICES

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Optical excitation and recombination of nonequilibrium charge carriers in GaAs doped superlattices are analyzed. Transformation of spontaneous radiative emission spectra under excitation is examined taking into account Gaussian tails of the density of states and screening of the fluctuated electrostatic potential. An influence of nonradiative defects on the lifetime of excited carriers is also investigated. A comparison of the numerical calculations with measured spectra of photoluminescence is carried out for the long-period superlattice structures having *i*-layers and with no *i*-layers. Certain difference in the recombination behavior occurs at low temperatures. The role of α -irradiation defects in the stabilization of the luminescence decay time is determined.

1 Introduction

Doped superlattices are proper for controllable semiconductor components. They are compatible with dense optical and electronic integration and could provide required performance characteristics of the devices. Unique features of the doped superlattices, or *n-i-p-i* crystals, are spatial separation of electrons and holes, tunable energy band gap, increased current carrier lifetime, wide variation of the potential profile and changing the electric and optical characteristics versus design parameters or added quantum wells and δ -doped layers [1, 2].

Earlier, the lifetime of charge carriers in GaAs superlattices was determined from the time-resolved photoluminescence spectra [3]. Changes in the total and radiative lifetimes were analyzed in the model with no $\mathbf{k}$ -selection rule and possible broadening effects. In spite of this, the predictions agree qualitatively with the observed increasing of the lifetime within the red shift of the decaying luminescence spectra.

In this paper, recombination processes of nonequilibrium charge carriers in the doped GaAs superlattices are examined. Self-consistent calculations of the electrostatic potential profile in the superlattices are presented. Transformation of electron energy levels and wave functions as well as variation of the overlap of

electron and hole wave functions under excitation as a function of the superlattice design parameters are considered in details.

2 Approach and results

The basic approach includes the following propositions. An influence of high doping on the energy spectrum and electron-hole recombination in *n-i-p-i* crystals is determined taking into account Gaussian fluctuations of the impurity concentration [4]. Generally, the fluctuations, correlation in the impurity distribution, and screening of the electrostatic potential have an effect separately in *n*- and *p*-regions [5].

The calculation of the tails appearing in the density of states allows to describe adequately the long-wavelength edge and transformation of the luminescence spectra and other peculiarities in optical and electric characteristics of doped superlattices. The Gaussian model of the tails [4] is to be more preferable than the usually used exponential approximation [6].

The major attention is given to the compensated GaAs superlattices with the layer thickness of 40 nm and concentration of donors and acceptors of 10^{18} cm^{-3} . The superlattice named No. 4i contains *i*-layers (*n-i-p-i* structure) and No. 4 means no *i*-layers (*n-p-n-p* structure). Both structures belong to the long-period doping superlattices and their photoluminescence properties were measured in a wide temperature range. Pronounced effects of α -irradiation were observed [7].

Redistribution of the space-charge of the excited carriers is presented in Fig. 1. Therewith at low temperatures, as seen in Fig. 2, the tunable photoluminescence band maximum $h\nu_{\text{max}}$ coincides with the difference of the quasi-Fermi levels ΔF , which in turn is close to the effective energy gap E_g' of the doped superlattice. At

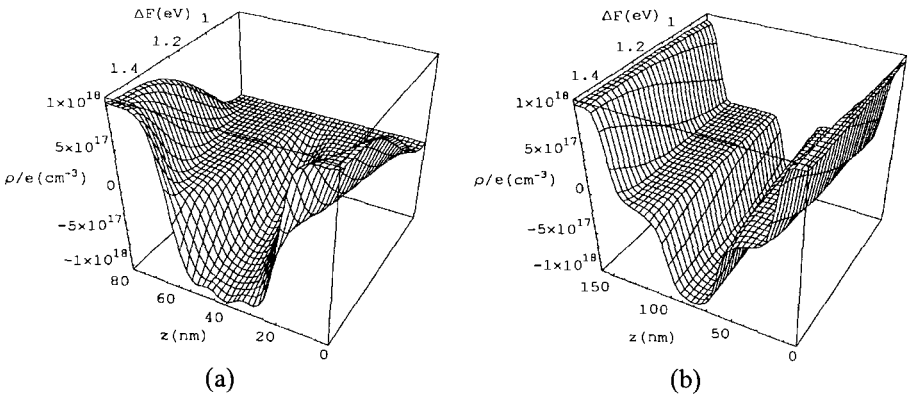


Figure 1. Space-charge distribution of the excited current carriers ρ along z -coordinate within one period of superlattice structures (a) No. 4 and (b) No. 4i as a function of the quasi-Fermi level difference ΔF at 20 K.

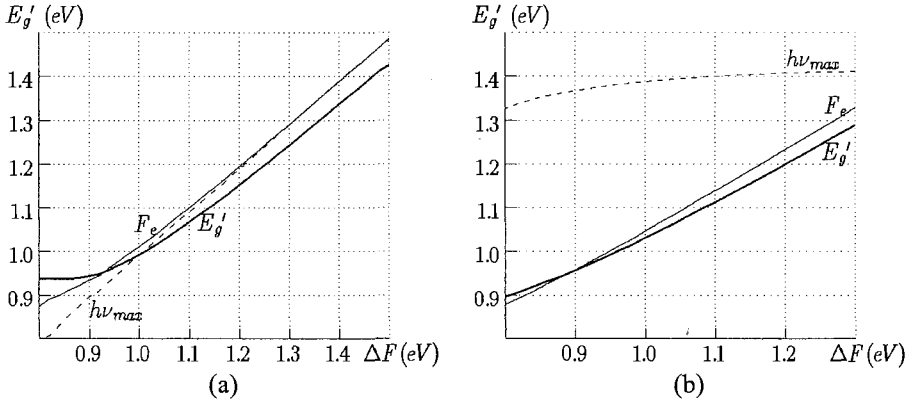


Figure 2. Dependence of the effective energy gap E_g' on the quasi-Fermi level difference ΔF in the superlattice No. 4 at 20 K (a) and 300 K (b). Thin curves represent the quasi-Fermi level for electrons F_e relative to the top of the valence band, dashed curves correspond to the quantum energy of the spontaneous recombination spectrum maximum $h\nu_{\max}$.

room temperature, the quantum energy $h\nu_{\max}$ is near the semiconductor band gap $E_g > E_g'$ and transformation of the emission spectrum under excitation comes practically to increasing the intensity.

Essential changes in the concentrations of charge carriers and accordingly in the potential profile and emission spectra are observed when the quasi-Fermi level difference ΔF exceeds, *e.g.*, for the superlattice No. 4 the value of 0.9 eV. Then, the chemical potential for electrons in the *n*-type layers becomes positive and the degeneration begins. For superlattice No. 4*i* it occurs at a smaller value of ΔF .

Results of calculations of the effective lifetime of nonequilibrium carriers τ are presented in Fig. 3. At room temperature, the radiative recombination lifetime τ_{sp}

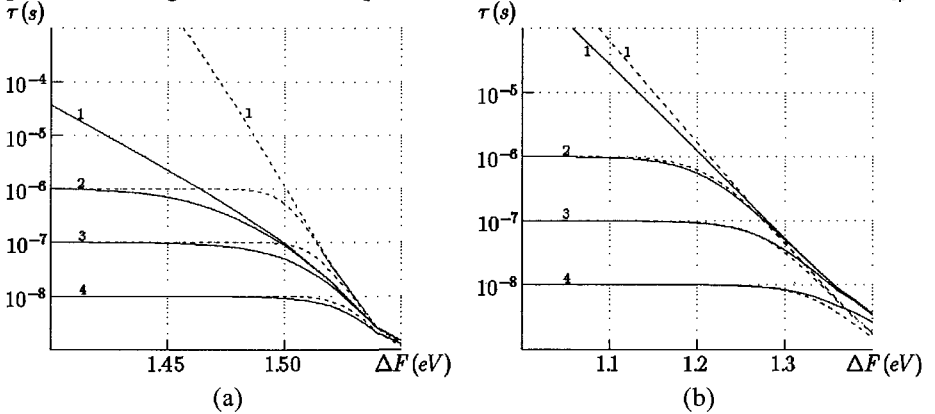


Figure 3. Lifetimes of charge carriers τ in superlattice structures (solid curves) No. 4 and (dotted curves) No. 4*i* versus the excitation level ΔF at 20 K (a) and 300 K (b). (1) $\tau_{nr} = \infty$, (2) $\tau_{nr} = 1 \mu s$, (3) $\tau_{nr} = 100 ns$, (4) $\tau_{nr} = 10 ns$.

falls up to 1 μ s at the excitation level $\Delta F = 1.2$ V. At low temperatures, the same value of τ_{sp} reaches at ΔF close to E_g .

Thus, in case of weak excitation the lifetime of electrons and holes is controlled, in general, by nonradiative recombination centers and equals to the corresponding value τ_{nr} . The effect of stabilization of the effective lifetime of charge carriers in homogeneously doped superlattices is more pronounced compared with δ -doped short-period superlattices [8]. Therewith, the role of defects occurs more essential in the structures with i -layers when the spatial removal of electrons and holes is larger. The measured decay time constant for tunable photoluminescence band in the α -irradiated GaAs doped superlattices lies in the interval from 7 to 12 ns [7], i. e., the value of τ_{nr} is of the order of 10 ns.

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SCATTERING MATRIX APPROACH TO LARGE-SCALE PHOTONIC CRYSTAL CIRCUITS

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We propose a scattering matrix approach to modeling of large-scale photonic crystal circuits and show that the transmission properties of complex circuits can be accurately calculated on the basis of scattering matrices of individual photonic crystal devices and waveguides which connect them. In addition, we show that functional devices such as waveguide bends generally exhibit a discontinuous frequency dependence in the phases associated with their complex reflection and transmission coefficients and emphasize its importance for the adequate modeling of photonic crystal circuits.

Over the past years, substantial research efforts have been directed at investigations of photonic crystals (PCs) with embedded defects such as microcavities and waveguides. These structures hold tremendous potential for the creation of large scale photonic integrated circuits which are required for the next generation of high-throughput optical communications systems. Indeed, recent experimental attempts to fabricate the simplest types of PC-based optical circuits are very promising [1].

Until now, the transmission properties [2] of PC-based circuits are mostly studied using the finite-difference time-domain (FDTD) method. This approach requires substantial computational resources and, as a consequence, modeling has been restricted to small-scale circuits. Another promising approach utilizes localized functions, such as localized defect modes [3,4] or photonic Wannier functions [5]. Such an approach combines accuracy with simplicity and provides intuitive insights into the properties of small-scale PC-based circuits [3-5]. In particular, PC-waveguides support not only propagating guided modes but also a number of evanescent guided modes which are crucial for the understanding of the properties of waveguide bends [3,4]. However, even this approach is quite involved when designing large-scale PC-based circuits.

In this paper, we suggest a novel approach to fast and accurate design of large-scale PC-based circuits. We show that such a circuit may be considered as a system of point-sized functional devices that are described by scattering matrices (S -matrices) and are connected by PC-waveguides with corresponding S -matrices. The properties of the entire circuit are then accurately described by recursively combining the individual S -matrices of the functional devices and the waveguides into a total S -matrix. It should be noted that there have been already suggestions to use S -matrix algorithms for modeling layered diffraction gratings [6] and small-scale integrated optical devices [7]. However, these algorithms are based on S -

matrices of tiny homogeneous slices which become computationally expensive for large-scale circuits.

To illustrate our approach, we consider PC-based circuits which consist of linear two-port devices, where we label any device (including waveguides) within this circuit by an index j . Furthermore, we denote the amplitudes of all guided modes (propagating and evanescent) between circuit elements $j-1$ and j by the p -component vectors u_j (modes propagating from device $j-1$ to device j) and d_j (modes propagating from device j to device $j-1$). Then, the behavior of device j is fully characterized by a matrix S_j , that connects incoming and outgoing modes:

$$\begin{pmatrix} u_{j+1} \\ d_j \end{pmatrix} = S_j \begin{pmatrix} u_j \\ d_{j+1} \end{pmatrix}, \quad S_j = \begin{pmatrix} T_j^{uu} & R_j^{ud} \\ R_j^{du} & T_j^{dd} \end{pmatrix}. \quad (1)$$

Here, the choice of letters T and R (transmission and reflection matrices) makes explicit the physical meaning of the four submatrices of S_j . Generally, the matrices S_j should be calculated numerically, for instance by the FDTD method [2], grating-based S -matrix algorithms [6,7], or from effective discrete equations [3-5]. However, for perfect non-absorptive PC-waveguides of length L and known dispersion relations $k_i(\omega)$ $i=1, \dots, p$ of the guided modes, the reflection matrices vanish, $R_{wg}^{ud} = R_{wg}^{du} = 0$, and the transmission matrices, T_{wg}^{uu} and T_{wg}^{dd} are diagonal.

$$T_{wg}^{uu} = (T_{wg}^{dd})^* = \begin{pmatrix} e^{ik_1(\omega)L} & 0 & 0 \\ 0 & \dots & 0 \\ 0 & 0 & e^{ik_p(\omega)L} \end{pmatrix}. \quad (2)$$

In the case of absorptive [7], finite-height [8], or disordered waveguides, their S -matrices become more complex and should be calculated explicitly.

The S -matrix of the entire circuit can then be calculated recursively from the S -matrices of the individual functional elements that make up the circuit. For instance, $S_c = S_a * S_b$ of a device c consisting of two sub-devices a and b with S -matrices S_a and S_b , respectively, is given by [6]

$$\begin{aligned} T_c^{uu} &= T_b^{uu} \left[1 - R_a^{ud} R_b^{du} \right]^{-1} T_a^{uu} \\ R_c^{du} &= R_a^{du} + T_a^{dd} R_b^{du} \left[1 - R_a^{ud} R_b^{du} \right]^{-1} T_a^{uu} \\ R_c^{ud} &= R_b^{ud} + T_b^{uu} R_a^{ud} \left[1 - R_b^{du} R_a^{du} \right]^{-1} T_b^{dd} \\ T_c^{dd} &= T_a^{dd} \left[1 - R_b^{du} R_a^{ud} \right]^{-1} T_b^{dd} \end{aligned} \quad (3)$$

The generalization of this S -matrix approach to multi-port PC-based circuits such as waveguide branches and add-drop filters is straightforward. In addition, if the individual devices are connected through sufficiently long waveguides, a very convenient approximation consists in neglecting the guided evanescent modes.

As an example, we consider a two-dimensional PC consisting of a square array (with lattice spacing a) of infinitely long dielectric rods (with radius $r=0.18a$ and dielectric constant $\epsilon=11.56$) in air. For TM-polarized light propagating in the plane of periodicity, this PC exhibits a large photonic bandgap for frequencies between

$\omega a/2\pi c=0.303$ and $\omega a/2\pi c=0.444$. By removing a row of rods, one can create a single mode PC-waveguide whose dispersion relation can be calculated using the supercell method. Waveguide bends can be constructed in a similar fashion and light transmission through a bend can be optimized [2].

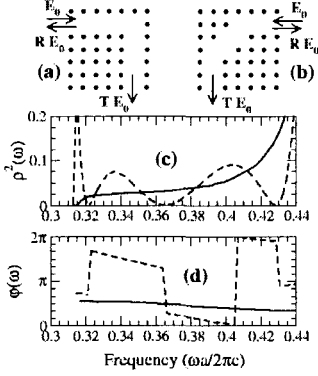


Figure 1. Geometries (a,b) of two different waveguide bends, whose complex reflection coefficients, $R(\omega)=\rho \exp(i\varphi)$, are characterized by the absolute value, $\rho(\omega)$, and phase, $\varphi(\omega)$, ((c) and (d), respectively) and have been calculated using effective discrete equations [3,4]. In (c) and (d), solid lines correspond to the bend (a) and dashed lines to the bend (b), respectively.

In Fig. 1, we display the frequency dependence of the complex reflection coefficients, $R(\omega)$, for two different bend geometries. In particular, the reflection amplitude $\rho(\omega)$ of the roundish bend (b) vanishes at several resonance frequencies and we want to emphasize that at exactly these resonance frequencies, the phase $\varphi(\omega)$ of the reflection coefficient experiences a non-trivial discontinuity. The complex transmission coefficients $T(\omega)$ display an analogous behavior and, together with the reflection coefficients $R(\omega)$, completely determine the bends' S -matrix if we neglect the evanescent modes as discussed above.

We now consider a system of two bends connected by a waveguide of length L , which is currently under intense experimental investigation [9]. Using FDTD calculations, it has been shown [10] that the transmission through a double bend structure may be quite different from that through a single bend. However, to the best of our knowledge, no systematic investigation of this issue has been carried out to date. Within the S -matrix approach, the transmission properties of a double bend structure follow directly from its S -matrix $S(\omega) = S_{bend}(\omega) * S_{wg}(\omega, L) * S_{bend}(\omega)$. In the present case, we can explicitly evaluate the transmission coefficient in terms of the single bend and waveguide parameters as

$$|T|^2 = \frac{[1 - \rho^2(\omega)]^2}{1 + \rho^4(\omega) - 2\rho^2(\omega)\cos[2k(\omega)L + 2\varphi(\omega)]}, \quad (4)$$

which coincides with the expression for transmission through a Fabry-Perot resonator with identical mirrors. In Figs. 2 and 3, we show the frequency dependence of the transmission T through double bend structures constructed from the bends of Fig. 1(a) and (b), respectively. The results obtained from direct numerical simulations [3,4] virtually coincide with the results of Eq. (4) using the

single bend and waveguide parameters only. In fact, we find that this agreement is practically exact for waveguide lengths $L > 3a$. Furthermore, we want to emphasize the importance of the phase $\varphi(\omega)$ in the complete characterization of a single waveguide. This is illustrated in Fig. 3, where we compare the results of Eq. (4) using the full phase information (solid line; see also Fig. 1(d)) with the results for a constant phase $\varphi(\omega)=0$. The inadequacy of disregarding the phase information is apparent.

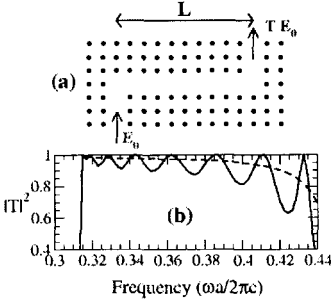


Figure 2. (a) A double bend system with bends of the type shown in Fig. 1(a) connected by a waveguide of length $L=10a$ and (b) the frequency dependence of the corresponding transmission T (solid line). For reference, the transmission through a single bend is shown (dashed line).

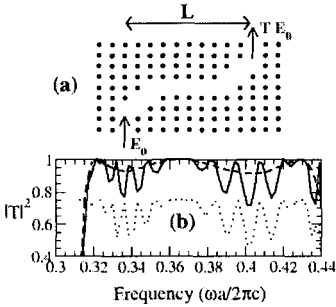


Figure 3. (a) A double bend system with bends of the type shown in Fig. 1(b) connected by a waveguide of length $L=20a$ and (b) the frequency dependence of the corresponding transmission T (solid line). For reference, the transmission through a single bend is shown (dashed line). The importance of the phase $\varphi(\omega)$ (see Fig. 1(d)) is illustrated by evaluating Eq. (4) for $\varphi(\omega)=0$ (dotted line; values for T have been shifted downward by 0.25).

In order to demonstrate the effect of neglecting guided evanescent modes, we compare in Fig. 4 the frequency dependence of the transmission T from numerical simulations (solid lines) with the results of Eq. (4) (dashed lines) for the double bend structure of Fig. 2 with reduced waveguide lengths, $L=a$ and $L=3a$, respectively. Upon increasing the bend separation from $L=a$ to $L=3a$, the evanescent mode coupling between the bends reduces substantially and excellent agreement between numerical simulations and Eq. (4) is restored.

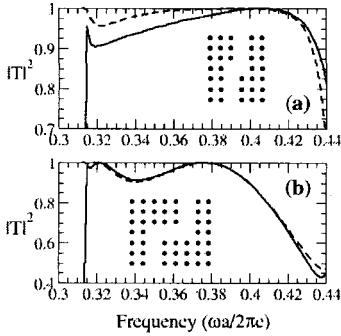


Figure 4. Frequency dependence of the transmission T for double bend structures similar to Fig. 2(a) with connecting waveguides of lengths $L=a$ (a) and $L=3a$ (b), respectively. Results of direct numerical simulations (solid lines) and results of Eq. (4) (dashed line) are shown.

In conclusion, we have introduced a S -matrix approach to the optical properties of large-scale PC-circuits. In this approach, an individual functional element is characterized by a S -matrix which allows efficient computation of the entire. We have applied this approach to double bend waveguiding structures and have obtained excellent agreement with direct numerical simulations.

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ASYMPTOTIC ANALYSIS OF RADIATION PATTERN OF A CLASSICAL DIPOLE IN A PHOTONIC CRYSTAL: PHOTON FOCUSING CAUSTICS

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An asymptotic analysis of radiation pattern of a classical dipole in a photonic crystal with an incomplete photonic bandgap is presented. Numerical examples and comparison with FDTD simulation are given for two-dimensional photonic crystals.

1 Introduction

Dielectric periodic media, also called photonic crystals, can possess a complicated photonic band structure, where allowed bands display strong dispersion and anisotropy [1]. Consequently, the electromagnetic energy flow inside a photonic crystal can be drastically modified from that in free space. Recently, there has been a growing interest in studies of energy flow inside photonic crystals. Being a strongly anisotropic material, a photonic crystal displays the beam steering effect [2,3]: the group-velocity direction does not necessarily coincide with the wave-vector direction. As a consequence, both the laser beam propagation inside the crystal and the emission of an optically active material placed within the crystal can reveal unusual properties.

We present an investigation an asymptotic form of electromagnetic power radiated by a classical point dipole located in two-dimensional photonic crystals possessing an incomplete photonic bandgap. We report redistribution of the energy flux inside the crystal. Within given approximation, the photon intensity from a point source in certain directions becomes infinite. These are directions in which the direction of the group velocity for one of the eigenstates is stationary with respect to a small variation in the wave-vector direction. We call this phenomenon *photon focusing* in analogy with similar effect known for acoustic phonons.

2 Asymptotic fields

We study a general linear, non-magnetic, dielectric medium with arbitrary periodic dielectric function, $\varepsilon(\mathbf{r}) = \varepsilon(\mathbf{r} + \mathbf{R})$, where $\mathbf{R} = \sum_i l_i \mathbf{a}_i$ is a vector of the direct Bravais lattice, l_i is an integer and $\mathbf{a}_i$ is a basis vector of the periodic lattice. We assume that an electromagnetic field is produced by a current source $\mathbf{J}$ and we take

the charge density $\rho \equiv 0$. For the periodic medium and the simplest form of a current density: $\mathbf{J}(\mathbf{r}, t) = \omega_0 \mathbf{d} \delta(\mathbf{r} - \mathbf{r}_0) e^{-i\omega_0 t}$, a harmonically oscillating point dipole with a frequency ω_0 and a real dipole moment $\mathbf{d}$, located at the position $\mathbf{r}_0$ inside a photonic crystal, one can find the following solution of the Maxwell's equations:

$$\mathbf{A}(\mathbf{r}) = \frac{4\pi c \omega_0}{V} \sum_n \int_{BZ} d^3 \mathbf{k}_n \frac{(\mathbf{a}_{nk}^*(\mathbf{r}_0) \cdot \mathbf{d})}{(\omega_{nk}^2 - \omega_0^2 - i\gamma)} \mathbf{a}_{nk}(\mathbf{r}) e^{i\mathbf{k}_n \cdot (\mathbf{r} - \mathbf{r}_0)}, \quad (1)$$

where $\mathbf{a}_{nk}(\mathbf{r})$ is a solution of a homogeneous wave equation.

We use the fact that in a typical experiment, $|\mathbf{r} - \mathbf{r}_0| \gg \lambda$, where λ is the wavelength of the electromagnetic wave. We follow here the evaluation presented for the asymptotic analysis of the Green's function of the phonon scattering problem [4] to show that the asymptotic form of the vector potential (1) at the position $\mathbf{r}$ far from the point dipole is given by [5]

$$\begin{aligned} \mathbf{A}(\mathbf{r}, t) \approx & i \sum_\nu \sum_n \exp\left(-i\left(\omega_0 t + \frac{\pi}{4}(\text{sign}(\alpha_1^\nu) + \text{sign}(\alpha_2^\nu))\right)\right) \\ & \times \frac{c}{V} \frac{(\mathbf{A}_{nk}^{\nu*}(\mathbf{r}_0) \cdot \mathbf{d}) \mathbf{A}_{nk}^\nu(\mathbf{r})}{|\mathbf{V}_{nk}^\nu|} \frac{8\pi^3}{|K_{nk}^\nu|^{1/2} |\mathbf{r} - \mathbf{r}_0|}, \end{aligned} \quad (2)$$

where $\mathbf{A}_{nk}^\nu(\mathbf{r}) = \mathbf{a}_{nk}^\nu(\mathbf{r}) e^{i\mathbf{k}_n^\nu \cdot \mathbf{r}}$ is the solution of homogeneous Maxwell's equations, $\mathbf{V}_{nk}^\nu$ is the group velocity and K_{nk}^ν determines the Gaussian curvature of the iso-frequency surface at $\mathbf{k}_n = \mathbf{k}_n^\nu$.

The amplitude of the vector potential in (2) is proportional to $|\mathbf{K}_{nk}^\nu|^{-1/2}$ and $|\mathbf{r} - \mathbf{r}_0|^{-1}$. Then a steady-state emission intensity far from a point dipole is given by the time averaged Poynting's vector $\mathbf{S}(\mathbf{r}) = (c/8\pi) \text{Re}[\mathbf{E}(\mathbf{r}) \times \mathbf{H}^*(\mathbf{r})]$ and it is proportional to the inverse Gaussian curvature of the iso-frequency surface, $|\mathbf{K}_{nk}^\nu|^{-1}$, and to the inverse square of the distance between a source and an observation point, $|\mathbf{r} - \mathbf{r}_0|^{-1}$. The asymptotic energy flux shows the necessary amount of decrease with distance, providing a finite value of the energy flux in any finite interval of a solid angle $d\Omega$, assuming non-vanishing Gaussian curvature of iso-frequency surface. A vanishing curvature formally implies an infinite flux along the corresponding observation direction. We will call this phenomenon *photon focusing* in analogy with similar effect known for acoustic phonons [6].

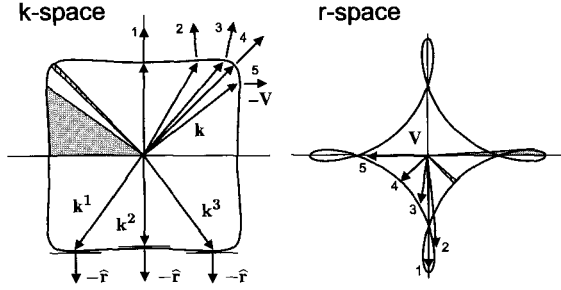


Figure 1. Iso-frequency and wave contours. Left: The central region of the iso-frequency contour of a square lattice photonic crystal. Right: Corresponding wave contour with folds. The shaded and cross-hatched regions show how two equal solid angle sections in coordinate space (right) map to widely varying solid angle sections in k -space (left). The wave and group velocity vectors with numbers illustrate the folds formation of the wave contour.

The physical picture of the phenomenon can be illustrated in the following manner. Fig. 1 left is an example of a part of the actual iso-frequency contour in a two-dimensional photonic crystal made out of dielectric rods placed in vacuum. Anisotropy of the crystal implies a complex non-spherical iso-frequency surface. A several waves can propagate in the given direction inside a photonic crystal. In the vicinity of the point with zero Gaussian curvature (parabolic point) an iso-frequency surface is flattened. That implies, that a very large number of eigenwaves with wave vectors in the vicinity of a parabolic point have nearly the same group velocity, contributing to the energy flux in the direction parallel to that group velocity. In Fig. 1, we illustrate this by the mapping of two equal solid angle sections along different observation directions in coordinate space into the corresponding solid angle sections in k -space. The cross-hatched solid angle section in coordinate space maps into a single smaller solid angle section in k -space implying a „defocusing“ of the energy flux. The shaded solid angle section in coordinate space, which crosses three different branches of the wave contour, maps into a larger solid angle section in k -space implying enhancement („focusing“) of the energy flux in this group velocity direction. This results in strongly varying angular distribution of emission intensity with sharp singularities (caustics).

3 Numerical example

In Fig. 2, a numerical example of the angular distribution of emission power radiated from the point source is presented for the case of a two-dimensional square lattice of air holes in a polymer. The energy flux is strongly anisotropic, showing a relatively small intensity in all directions except along directions associated with parabolic points of iso-frequency surface, where the intensity tends to infinity. Predictions of asymptotic analysis on far-field radiation pattern (2) are substantiated with FDTD calculations, revealing a reasonable agreement (Fig. 2, left).

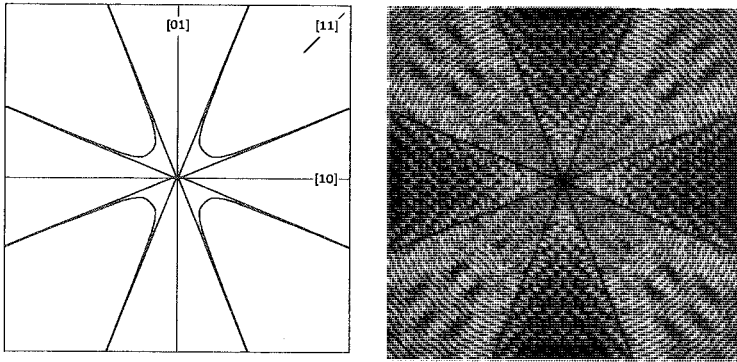


Figure 2. (Left) An asymptotic far-field radiation pattern of a classical dipole inside a 2D polymer photonic crystal for a frequency within a stopband, averaged over a dipole moment orientation. (Right) FDTD simulation of the steady-state Poynting vector distribution for the same structure as in the left panel. Black lines are the asymptotic directions of energy flux. The structure contains an array of 50x50 holes in a typical polymer ($n=1.56$) matrix subjected to perfect match layer (PML) boundary conditions. A monochromatic point source excitation is positioned at the center of the modeled area.

Acknowledgements

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CONSERVATION LAWS FOR THE INTEGRATED DENSITY OF STATES IN ARBITRARY QUARTER-WAVE MULTILAYER NANOSTRUCTURES

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A conservation rule is established that restricts the integrated dimensionless modified density of states for wave propagation in arbitrary quarter-wave multilayer structures in analogous way to the Barnett-Loudon sum rule for modified spontaneous emission rate.

1 Introduction

Many optical phenomena are known to be strongly modified inside complex inhomogeneous media if the size of the inhomogeneities is of the same order of magnitude as the wavelength for the light involved in the process. For example, photonic band gap nanostructures have obtained their name due to the fact that they strongly suppress the propagation of any wave whose wavelength is inside a certain region called a *photonic band gap* (PBG). Other wave properties that are subjected to modification inside PBG structures are spontaneous emission, Planck blackbody radiation, and Raman scattering.

However, the degree of modification we can exert on the properties of optical phenomena by introducing a complex medium appears to be limited. These limits, called *conservation* or *sum rules*, seem to have fundamental physical reasons. For instance, the Barnett-Loudon sum rule [1] places a restriction on the modification of spontaneous emission rate *regardless* of the means used and is derived from the general causality-related laws such as the Kramers-Kronig relation.

In this paper, we report an analogous conservation rule for the wave propagation through an *arbitrary* one-dimensional PBG structure. This rule restricts the modification of optical spectra for such structures regardless of their topological properties, as it is derived from general dispersion relations.

2 Quarter-wave multilayer nanostructures

In this paper we consider plane wave propagation inside multilayer structures containing layers of equal optical path, i.e., in an N -layer stack

$$n_1 d_1 = n_2 d_2 = n_i d_i \equiv \frac{\lambda_0}{4} = \frac{\pi c}{2\omega_0}, \quad i = 1, 2, \dots, N. \quad (1)$$

Here ω_0 is called *central frequency*, and (1) is called the *quarter wave (QW) condition*. It is important that the optical spectra of *any* structure conforming to (1) is periodic in the frequency scale with the period equal to ω_0 [2]. This periodicity provides a natural way of frequency normalization and makes it enough to analyze a fixed region of the spectrum for any structure. Besides, in each period there is a mirror symmetry around the odd multiples of ω_0 :

$$T[(2n+1)\omega_0 - \Delta\omega] = T[(2n+1)\omega_0 + \Delta\omega], \quad 0 < \Delta\omega < \omega_0. \quad (2)$$

In addition, in most cases we will consider *binary* structures, i.e., those containing only two kinds of layers, denoted with binary digits 0 and 1. However, as it will be shown later, this requirement is insubstantial to the major result of this paper, and is introduced only for simplicity reasons.

3 Conservation rules for the density of states

Prior to proceeding with the major result of this paper, we will briefly touch upon another important relation that is related to the sum rule for eigenstates. During our investigation of spectral properties of complex-topology multilayers [2] we noticed that the number of transmission peaks (always present in the spectra of multilayers) for any QW multilayer *equals the number of layers* N . This has been numerically verified to be true for all possible structures with the same N . Some illustrative examples can be found in Fig. 1.

3.1 Density of modes

Although the number of peaks per period is conserved for any QW multilayer, one can see in Fig. 1 that some peaks are very sharp while others are substantially suppressed.

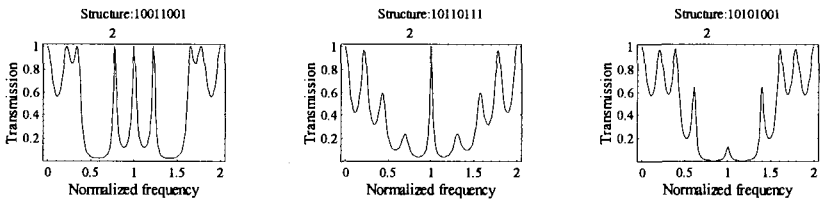


Figure 1. Transmission spectra of several 8-layer QW multilayer structures. One period is depicted. It can be seen that in each plot there are 8 (more or less pronounced) resonance transmission peaks.

One way to establish a stricter conservation rule is to replace transmission by the *density of modes* (DOM) introduced according to [3] as

$$\rho(\omega) \equiv \frac{dk(\omega)}{d\omega} = \frac{1}{D} \frac{y'x - x'y}{x^2 + y^2}, \quad t \equiv x + iy. \quad (3)$$

It must be noted here, however, that the use of the term ‘density of modes’ for expression (3) is a subject of actual discussion, and the strict concept of the DOM for such systems (possessing continuous or quasidiscrete rather than discrete spectra) is yet to be introduced. However, the quantity in (3) *does* possess some properties of the DOM and can be taken as a phenomenological definition.

Since we are interested in the modification of DOM in multilayers, it is reasonable to normalize this quantity to the “bulk velocity” of light in the structure.

For a binary multilayer (N_0 and N_1 being the number of corresponding layers in the structure, $N=N_0+N_1$), the normalized DOM has the form

$$\tilde{\rho}(\eta) \equiv \rho(\omega) v^{(\text{bulk})}, \quad \eta \equiv \frac{\omega}{\omega_0}, \quad v^{(\text{bulk})} \equiv \frac{D}{\tau} = \frac{N_1 n_0 + N_0 n_1}{N n_1 n_0}. \quad (4)$$

3.2 Conservation of the integrated normalized density of states

As a result of numerical verification analogous to those of Section 3.1, we have established that *the integral over the interval of normalized frequencies $[0, 2]$ of the quantity in (4) equals 2 for any binary multilayer structure*:

$$\int_0^2 \tilde{\rho}(\eta) d\eta = 1. \quad (5)$$

Further research revealed that this relation can be derived analytically from the dispersion relation for QW multilayer structures. Indeed, substituting (3) and (4) into (5) with doubled upper integration limit, we get

$$\mathfrak{I} \equiv \int_0^2 \rho(\eta) v^{(\text{bulk})} d\eta = \frac{1}{\omega_0} \int_0^{2\omega_0} \rho(\omega) v^{(\text{bulk})} d\omega = \int_{k(0)}^{k(2\omega_0)} v^{(\text{bulk})} dk(\omega). \quad (6)$$

The “effective wave number” k is related to the frequency ω by the dispersion relation, D being the total *physical* thickness of the structure:

$$\tan k(\omega) D = y(\omega)/x(\omega) = \tan \varphi, \quad t \equiv x + iy \equiv \sqrt{T} e^{i\varphi}. \quad (7)$$

Here, the phase φ is the total phase accumulated by the wave as it propagates through the structure. Since all layers are quarter-wave, no internal reflection occurs at the even multiples of ω_0 , which immediately makes it possible to calculate the phase ($D^{(\text{opt})}$ being the total *optical* thickness of the structure)

$$\varphi[2\omega_0] = D^{(\text{opt})} \cdot 2\omega_0/c = 2 \cdot \frac{2\pi}{\lambda_0} \cdot N \frac{\lambda_0}{4} = N\pi. \quad (8)$$

Substituting (8) and (7) into (6), after some simple algebra we get $\mathcal{I} = 2$, which fully agrees with (5) if we take into account the symmetry condition (2).

4 Discussion

To summarize, we have found that there is a relation that holds for *any* (not necessarily binary, as can be seen from the previous section) QW multilayer structure and places a restriction on the DOM integrated over a certain frequency region. Taking into account that the dependence $\rho(\omega)$ itself, like the transmission spectrum $T(\omega)$, *does* strongly depend on the topological properties of the structure (cf. Fig. 1), it can be inferred that *indeed, we have found a conservation rule, which seems to be a general property of a wave propagation.*

The physical meaning of this rule is straightforward: whatever the media is and however modified the DOM spectrum, *we can only redistribute the DOM across the spectrum and can **not** by any means alter the total quantity of states for an electromagnetic wave.* This restriction is similar to that implied in the Barnett-Loudon sum rule [1].

Moreover, for quarter-wave multilayers we can formulate another important result: the rule (5) *explicitly gives the frequency interval over which we can control the DOM redistribution.*

Finally, we would like to point out what will happen if the structure is not QW and the condition (1) no longer holds. Here, two cases have to be distinguished. If the optical lengths of all layers are *commensurate*, i.e., each of them can be expressed as integer multiples of *some* non-zero quantity $\lambda'_0/4$, then everything that will change is the upper integration limit in (5). If, however, the layers are *incommensurate* (which is equivalent to say that $\lambda'_0 \rightarrow 0$), then integration has to be performed over the whole spectrum, on analogy to the Barnett-Loudon rule.

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PECULIARITIES OF LIGHT TRANSFORMATION IN FINITE THREE-LAYERED PERIODIC NANOSTRUCTURES

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Correct analytical expressions are obtained for reflection and transmission coefficients of a finite three-layered periodic structure. An enhancement of light energy localization inside the structure simultaneously at all transmission resonance frequencies, is shown.

Well investigated stratified periodical structures (SPSs) are widely used as dielectric mirrors, polarization devices for integrated optics, tunable narrow band filters, time delay devices, nonreciprocal elements, devices of parametric and non-linear optics [1]. The two-layer SPSs are a particular case of more general class of three-layer structures. For example, the three-layered structures **(ABB):N** with layers **A** and **B** and number of periods N can be considered as a two-layer SPS. In the paper we present features of optical wave transformation in three-layer periodical structures.

Consider a normal light transmission through a finite isotropic three-layer periodical structure, made of identical layers indicated by numbers 1, 2 and 3 with a thickness d_1 , d_2 and d_3 and refraction indexes n_1 , n_2 and n_3 , respectively. Let this SPS with N periods to be surrounded by isotropic dielectric media with refraction indexes n_0 and n_4 (Fig. 1).

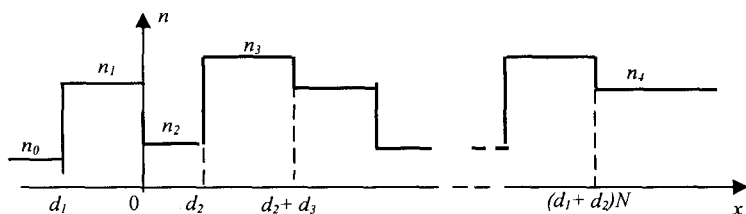


Figure 1. A three-layer periodical dielectric structure.

As well known, the electric field intensity with polarization vector $\mathbf{e}$ in the periodical structure is presented by a superposition of Floquet-Bloch waves propagating in direct and opposite directions [2]:

$$\mathbf{E}(x) = (C_1 E_1(x) + C_2 E_2(x)) \mathbf{e}, \quad (1)$$

where C_1, C_2 are constants, $E_{1,2}(x) = E_{1,2}(x + D)$ are periodic functions with the period $D = d_1 + d_2 + d_3$. The expression for amplitudes $E_{1,2}(x)$ in layers 1, 2 и 3 of the first period reads

$$E_{1,2}^{(1)}(x) = G_{1,2}^{(1)} \cos(k_0 n_1 x + \varphi_{1,2}^{(1)}), \quad E_{1,2}^{(2)}(x) = G_{1,2}^{(2)} \cos(k_0 n_2 x + \varphi_{1,2}^{(2)}), \\ E_{1,2}^{(3)}(z) = G_{1,2}^{(3)} \cos(k_0 n_3 (x - d_2) + \varphi_{1,2}^{(3)}).$$

Taking into account the periodicity of functions included in (1) $E^{(i)}(x) = \exp(i\xi) E^{(i)}(x - D)$ and using conditions of continuity for a function $E^{(i)}(x)$ and its derivative in points $z = 0, z = d_2, z = d_2 + d_3$, and also condition of continuity of electrical and magnetic field vectors at boundaries $z = -d_1$ and $z = ND - d_1$, we have obtained reflection ρ' and transmission τ' coefficients of the structure at normal incidence of light wave at the boundary $z = -d_1$:

$$\rho' = \frac{(n_1 s_1 + i n_4 c_1)(n_0 c_2 - i n_1 s_2) \exp(i\xi N) - (n_1 s_1 + i n_0 c_1)(n_4 c_2 - i n_1 s_2) \exp(-i\xi N)}{(n_1 s_1 - i n_0 c_1)(n_4 c_2 - i n_1 s_2) \exp(-i\xi N) + (n_1 s_1 + i n_4 c_1)(n_0 c_2 + i n_1 s_2) \exp(i\xi N)}, \quad (2a)$$

$$\tau' = \frac{2(c_2 s_1 - c_1 s_2) n_1 n_0}{(n_1 s_1 - i n_0 c_1)(n_4 c_2 - i n_1 s_2) \exp(-i\xi N) + (n_1 s_1 + i n_4 c_1)(n_0 c_2 + i n_1 s_2) \exp(i\xi N)}, \quad (2b)$$

where $c_{1,2} = \cos(-k_0 n_1 d_1 + \varphi_{1,2}^{(1)})$, $s_{1,2} = \sin(-k_0 n_1 d_1 + \varphi_{1,2}^{(1)})$,

$$\varphi_{1,2}^{(1)} = \arctan([(-a_2 \pm \sqrt{a_2^2 - 4a_1 a_3}) / 2a_1];$$

$$a_1 = n_1(t_1 t_2 t_3 n_3^2 - t_3 n_2 n_1 - t_2 n_1 n_3 - t_1 n_2 n_3), \quad t_{1,2,3} = \operatorname{tg}(k_0 n_{1,2,3} d_{1,2,3}),$$

$$a_2 = n_2 n_1 t_3 (t_1 n_1 - t_2 n_2) - n_3 t_3^2 (t_1 n_2 - t_2 n_1) + t_1 t_2 n_3 (n_1^2 - n_2^2),$$

$$a_3 = n_2 (t_1 t_2 t_3 n_1 n_2 - t_2 n_2 n_3 - t_1 n_1 n_3 - t_3 n_3^2),$$

and dispersion equation

$$\cos \xi = [(n_1 - n_3)(n_2 + n_3)(n_2 - n_1) \cos(k_0(n_1 d_1 - n_2 d_2 - n_3 d_3)) \\ - (n_2 - n_1)(n_2 - n_3)(n_3 + n_1) \cos(k_0(n_1 d_1 - n_2 d_2 + n_3 d_3)) \\ - (n_1 - n_3)(n_2 - n_3)(n_2 + n_1) \cos(k_0(n_1 d_1 + n_2 d_2 - n_3 d_3)) \\ + (n_3 + n_1)(n_2 + n_3)(n_2 + n_1) \cos(k_0(n_1 d_1 + n_2 d_2 + n_3 d_3))] / (8n_1 n_2 n_3).$$

Formula (2) contain as a particular case the formula for transmission and reflection coefficients of a two-layer structure [2].

Knowledge of the transmission coefficient τ' allows to obtain an optical density of states (the magnitude which is inverse to group velocity of light in the structure $\eta(\omega) = dk / d\omega$) [4]:

$$\eta(\omega) = \frac{dk}{d\omega} = \frac{1}{DN} \frac{\tau_x d\tau_y / d\omega - \tau_y d\tau_x / d\omega}{\tau_x^2 + \tau_y^2}, \quad (3)$$

where $\tau_y = \text{Im}(\tau')$, $\tau_x = \text{Re}(\tau')$.

On the basis of the obtained expressions (2-3) we have considered peculiarities of light transformation in a three-layer SPS. In Fig. 2 one can see the transmission spectrum of SiO_2/GaAs , formed as follows: $(\text{BA}_2\text{A}_1):5$ (two-layer SPS) and $(\text{A}_1\text{BA}_2):5$ (three-layer SPS). Here A_1 and A_2 are quarter and half-wave layers of GaAs, correspondingly, B is quarter wave layers of SiO_2 at a wavelength $\lambda = 0.6 \mu\text{m}$. The interference transmission spectra of two- and three-layer structures are notably different. The spectrum of SPS $(\text{A}_1\text{BA}_2):5$ is characterized by considerable contrast and small width of transmission maxima arranged between the first and the second (second and third) photonic bandgaps. In this case, structure (A_1BA_2) can be represented as two-layer (BA_2A_1) , which has cap and buffer layers playing a role similar to a Fabry-Perot resonator.

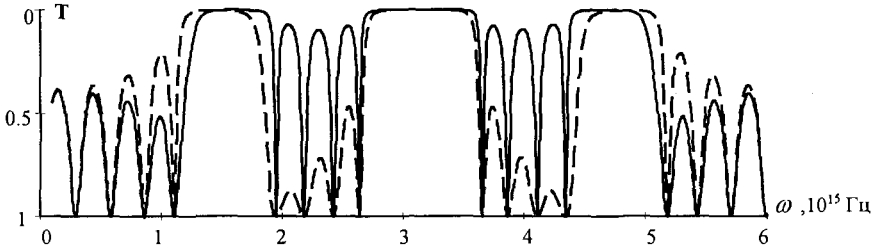


Figure 2. Transmission spectrum for SiO_2/GaAs structure, created as $(\text{BA}_2\text{A}_1):5$ (dashed line) and $(\text{A}_1\text{BA}_2):5$ (solid line).

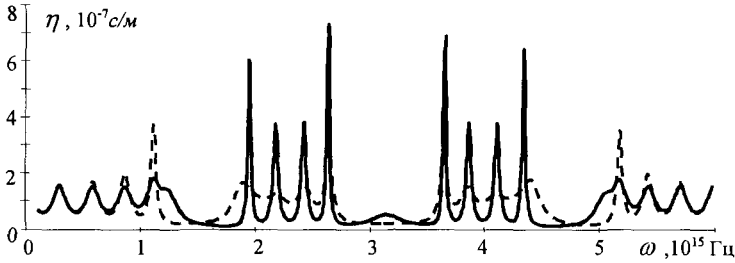


Figure 3. Density of optical states for SiO_2/GaAs structure, created as $(\text{BA}_2\text{A}_1):5$ (dashed line) and $(\text{A}_1\text{BA}_2):5$ (solid line).

The spectrum of the optical density of states $\eta(\omega)$ for SiO_2/GaAs structure, calculated according to (3) is shown in Fig. 3. On can see that density of states in the three-layer SPS $(\text{A}_1\text{BA}_2):5$ is 2.5 times higher than that in the two-layer structure $(\text{BA}_2\text{A}_1):5$. The increased optical density of states is accompanied by an enhancement of the light energy localization inside the structure (see Fig. 4) and

reduction of the group velocity of light in the SPS. As a result (see Fig. 3), light energy localization inside $(A_1BA_2):10$ is 7 times higher than that inside $(BA_2A_1):10$. It enables to observe simultaneously at all transmission resonances the enhancement of optical nonlinearity [3] and light delay phenomenon [4].

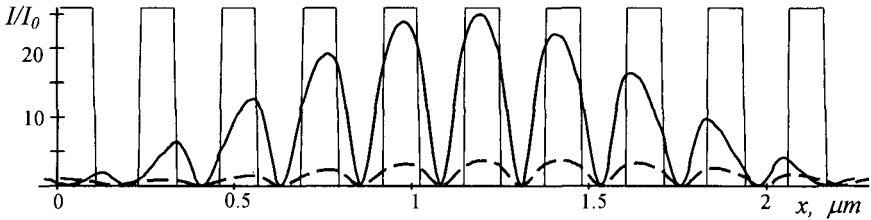


Figure 4. Intensity distribution I/I_0 inside structure $SiO_2/GaAs (BA_2A_1):10$ (dashed line) and $(A_1BA_2):10$ (solid line) at normal incidence of light wave of intensity I_0 and frequency $\omega = 1842 \cdot 10^{15}$ Hz.

In conclusion, the correct analytical expressions have been derived for transmission and reflection coefficients of a three-layer periodic structure surrounded by two different isotropic dielectric media. On the basis of the given formulas it was shown that for three-layer SPS it is possible to realize the enhancement of resonant interaction of light with the structure. By this way one can achieve an increased light energy localization inside the structure and decreased group velocity of light inside SPS. It is necessary to point out that the enhancement of these phenomena is put into practice by using quasi-periodic structures. The possibility to enhance the resonant phenomena by the use of finite periodic structure, optical properties of which are predictable, easily calculated and practically realizable, opens wide perspectives for their application.

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LASER PULSE COMPRESSION IN FIBONACCI MULTILAYER NANOSTRUCTURES

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A specific feature of multilayer quasiperiodic structures, namely, the inequality of the numbers of constituent layers of different type in a binary Fibonacci structure, allows to increase dispersion in comparison with periodic multilayers of the same length. Taking it into account, we have studied femtosecond light pulse compression in quasiperiodic non-symmetric and symmetric Fibonacci-like structures. The theoretical analysis has shown that non-symmetric Fibonacci structures are more promising for the compressor design than periodic stacks. One of such advantages is decrease of laser pulse compression length in a quasiperiodic structure which allows to reduce the geometrical size of a compressor by ten times (compared to periodic stacks) if the refraction index difference is large enough.

1 Introduction

Designing ultrashort pulse compressors is of great interest nowadays for modern femtotechnologies. Photonic band gap (PBG) crystals provide an opportunity to control the phase of short light pulses and to compress them. Eggleton with co-workers [1] was the first to experimentally demonstrate the possibility of pulse compression in optical fiber Bragg gratings with Kerr nonlinearity, although this compression effect has been theoretically predicted earlier [2].

However, investigations of pulse propagation in PBG structures have been mainly restricted to picosecond pulses [3, 4]. At this time scale the approximation of slowly varying envelopes is applied. In order to study the possibilities of using PBG structures to control parameters of ultrashort (i.e., femtosecond scale) laser pulses, we can no longer use this approximation and have to choose an adequate numerical scheme to simulate the pulse propagation. Such simulations can be carried out with the transfer-matrix approach in combination with Fourier analysis. If the PBG structure is nonlinear, then nonlinear finite-difference time-domain technique is required. Using this technique, several groups revealed [5, 6] that both linear and nonlinear periodic PBG structures compress short laser pulses at submillimeter distance. The authors in [7] experimentally demonstrated the femtosecond laser pulse compression effect in a linear PBG structure with dimensions of the order of

several microns if the refraction index modulation is high. However, the limits on the structure size for linear and nonlinear cases, as well as on the parameters of ultrashort pulses compressed using PBG structures, remain in question. At present this problem has mainly been studied with respect to periodic PBG structures.

The present paper is devoted to the theoretical analysis of laser pulse compression in quasiperiodic Fibonacci-like structures.

2 Peculiarity of Fibonacci structures

The Fibonacci multilayer structures belong to the class of deterministic non-periodic media. They are quasiperiodic structures because they include several incommensurate periods. Multilayer binary Fibonacci stacks of n -th stage are recurrently generated by the following rule:

$$F_n = \{F_{n-2}, F_{n-1}\}, \quad n = 2, 3, \dots, F_1 = \{AB\}. \quad (1)$$

Layers A and B themselves are two initial elements in the Fibonacci sequence.

We note that many non-periodic structures, including Fibonacci ones, have a specific feature, which consists of the following. The constituent layers (A and B) of different optical density (and hence different thickness) occur in different number inside the structure, contrary to periodic multilayers. When the number of optically more dense layers is greater than that of optically less dense ones, the overall thickness diminishes compared to periodic stack with the same number of layers. This allows to place more layers into the same thickness which results in an increase of dispersion in Fibonacci structures in comparison with periodic ones of the same length as will be shown below.

3 Group-velocity dispersion in Fibonacci multilayers

As follows from the second dispersion-theory approximation, the distance L_{compr} at which the duration of a chirped laser pulse reaches its minimum is defined by the dispersion-spreading length L_{disp} of a wave packet:

$$L_{\text{compr}} = \frac{\alpha_0 \tau_0^2}{1 + (\alpha_0 \tau_0^2)^2} L_{\text{disp}}, \quad (2)$$

where τ_0 and α_0 are the duration and chirp of phase modulated pulse. Increase of group-velocity dispersion $k_2 = \partial^2 k / \partial \omega^2$ makes it possible to diminish dispersion length. Maximum value of group-velocity dispersion is realized at band gap edges of the structure under study. As can be seen from Fig. 1a and 1b, group-velocity dispersion for a Fibonacci structure of 6-stage which is composed of 13 ZnS layers (with refraction index $n_1 = 2.3$ and thickness $l_1 = 83.6$ nm) and 8 cryolit layers

($n_2=1.35$, $l_2=142.5$ nm), is greater by 3 times in comparison with a periodic stack (10 layers of ZnS and 10 layers of cryolit) of the same length. Rise of k_2 is stronger when Fibonacci structure has fewer number of layers. Fig. 1c and 1d illustrate the frequency dependence of group-velocity dispersion for Fibonacci structure of 4-stage (5 layers of ZnS and 3 layers of cryolit) and periodic stack (4 layers of ZnS and 4 layers of cryolit) of the same length. The value of k_2 for Fibonacci multilayers is larger by ten times as compared to periodic. A rise in the refraction index difference of constituent layers to a value greater than 0.95 enables us to realize the better prevalence of Fibonacci stack over periodic.

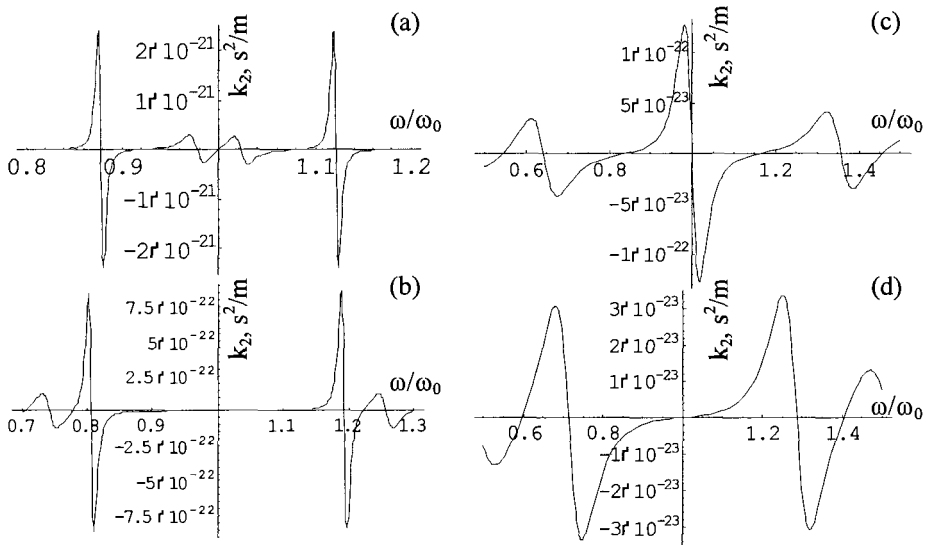


Figure 1. Frequency dependence of group-velocity dispersion for Fibonacci stacks of 6-stage (a), of 4-stage (c) and for periodic structures (b), (d) of the same length as corresponding Fibonacci stack. Normalization frequency $\omega_0 = 2.45 \cdot 10^{15} \text{ s}^{-1}$ corresponds to quarter-wave constituent layers.

Thus the theoretical analysis has shown that the Fibonacci multilayer structures are more promising for the compressor design as compared to the periodic stacks. One of the main advantages of compressors based on one-dimensional linear Fibonacci structures is that the length of dispersion spreading for chirped light pulses is ten times less than that for periodic structures of the same size. This fact results in the corresponding decrease of compression depth, which makes it possible to reduce the minimal size of chirped optical pulses compressor in exactly the same manner. It is also worth noting that Fibonacci structures under study are non-symmetric. Symmetric modified Fibonacci structures which are obtained by stripping the first two layers from the stack generated by Fibonacci law (1) do not exhibit such an advantage over periodic stacks of the same length.

4 Conclusion

Deterministic non-periodic Fibonacci structures have a specific feature not present in periodic ones. Quarter-wave Fibonacci multilayers can contain more layers than periodic ones on the same length scale because they can have more layers with high index of refraction which are geometrically thinner. This allows to increase the dispersion of the structure and to decrease geometrical compression length for optical chirped pulses. Theoretical analysis has shown that this diminish can amount to as much as 10 times (compared to periodic stacks) if the refraction index contrast is high. Therefore these structures can minimize the size of compressors for chirped optical pulses.

Acknowledgements

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SYNTHESIS OF THIN FILM TITANIA PHOTONIC CRYSTALS THROUGH AN INFILTRATING SOL-GEL PROCESS

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Large-area high-performance thin film titania photonic crystals have been prepared through an infiltrating sol-gel process using a silica colloidal crystal template. The effects of the immersion time, the withdrawal rate and the number of dips on the morphology and the photonic properties of the film were studied. It was found that by carefully choosing all the parameters, a high filling fraction and a good surface quality could be obtained.

1 Introduction

Recently, important efforts have been made to fabricate photonic crystals by colloidal crystal templating [1-5]. Colloidal crystals are self-organized arrays of silica or latex spheres, having the periodicity required for photonic band gaps. The basic idea is to use a colloidal crystal as a template, infiltrate the interstitial spaces between the spheres with another material and, then, remove the spheres by chemical etching or combustion. Since the resulting macroporous structures have a complete photonic bandgap [6,7], these materials have many applications in photonics.

Calculations have shown that a high refractive index and a suitable filling fraction are critical for the photonic properties of the highly-ordered macroporous structures.

In this paper, a new infiltrating sol-gel technique allowing to fill the voids of the silica template efficiently, is presented. The effect of the immersion time, the withdrawal rate and the number of dips on the filling fraction and the morphology of the surface layer were studied. Titania was used as infiltrating material due to its high refractive index and minimal absorption at visible wavelengths. The large centimeter-sized samples obtained through this method allowed the measurement of the photonic properties under different conditions of preparation. A reflection-transmission photoellipsometer [8] developed in our laboratory was used to measure the transmission spectra of the samples at normal incidence in the range of 300-800 nm.

2 Results and discussion

Fig. 1 shows transmission spectra measured at normal incidence for two samples prepared with two different immersion times.

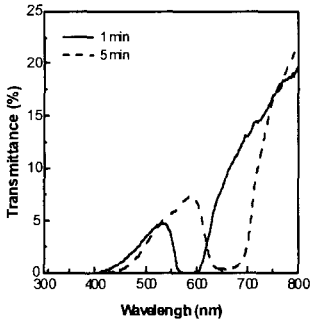


Figure 1. Transmission spectra at normal incidence of samples prepared with different immersion times (relative withdrawal rate 2500, 10 dips).

It can be seen that when the immersion time is longer, the transmission minimum is deeper and it appears shifted to longer wavelengths showing an increase in the filling fraction. However, the immersion time should not be longer than 5 min, otherwise the surface layer will be too thick.

The rate with which the template is drawn out of the sol is one of the most critical factors in the structure-formation process. Fig. 2 shows the transmission spectra at normal incidence for samples prepared with different withdrawal rates.

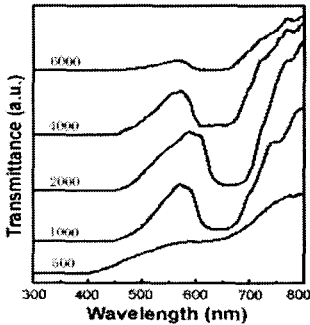


Figure 2. Transmission spectra at normal incidence of samples prepared with different withdrawal rates (immersion time 5 min, 10 dips).

It can be seen that with increasing the relative rate from 500 to 2000, the transmission dip deepened and shifted towards longer wavelengths. However, when the drawing rate was too high, the transmission dip became shallower and shifted again to shorter wavelengths. To understand this behavior, we have to consider the effects of the drawing rate on both the filling and the surface-coating processes. In both cases, the quantity of material left on the surface or inside the voids is

determined by the rate of the gelation of the sol. The faster the gelation is, the thicker the film or higher the filling fraction will be. The gelation of the sol on the surface is determined by the withdrawal rate. The gelation inside the voids is decided by the drawing rate and the surface layer which would block the air and delay the gelation. When the withdrawal rate is slow, the surface layer is too thin to influence the gelation inside the voids, and the filling fraction will increase with the rate. When the thickness of the surface layer increases, the delay of the gelation becomes more important, and will finally exceed the effect of the withdrawal rate, resulting in a decrease of the filling fraction.

Fig.3 shows the SEM surface images of samples prepared with different withdrawal rates.

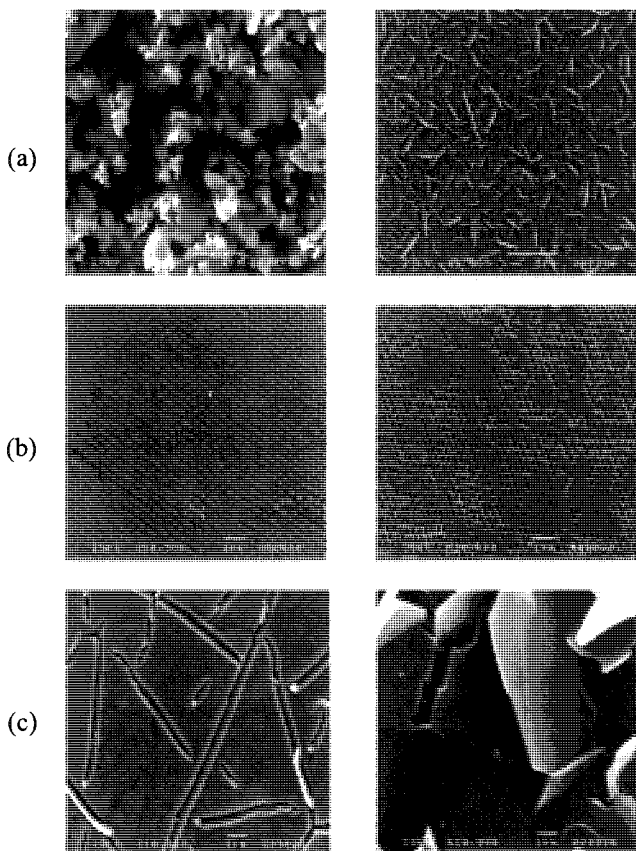


Figure 3. SEM surface images of the titania-opal composites (left) and the corresponding titania inverted opals (right) with different withdrawal rates (a) 500, (b) 2000, (c) 6000 (immersion time 5 min., 10 dips).

The left images show the composites, and the right ones the macroporous titania structures. It can be seen that the rate affects the surface structures dramatically. At a high withdrawal rate (6000), the surface layer is thick and heavy resulting in a diffuse surface (Fig. 3c). At a low rate, (500), the layer is fragile and, may be damaged during the repeated dipping and withdrawal process, resulting in a fragmentary surface (Fig. 3a). At a rate of 2000, the thickness of the surface layer is appropriate and a smooth surface structure can be seen (Fig. 3b). The surface titania layer helps to reinforce and flatten the surface of the template.

3 Conclusion

An infiltrating sol-gel technique was developed to fabricate large-area high-performance titania photonic crystals. It was found that by carefully choosing the parameters of the infiltrating process, both a high filling fraction and a good surface quality can be obtained, which results in strong photonic properties in the transmission spectra.

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FTIR STUDY OF VERTICALLY ETCHED SILICON AS 1D PHOTONIC CRYSTAL

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The reflection spectra of grooved silicon and grooved silicon infiltrated with nematic liquid crystal (LC) have been calculated. The grooved silicon structures with different lattice constants ($A=16, 12, 8$ and $4 \mu\text{m}$) have been designed and fabricated. The analysis of the polarised infrared spectra of Si structures infiltrated with LC allows one to determine the refractive index (N_{LC}) and the orientation of the liquid crystal.

1 Introduction

The photonic crystals (PCs) are materials with a regular change in the refractive index, N , with periodicity of the photon order of the wavelength [1]. The ratio of the refractive indices of the different layers (so called optical contrast) in the 1D dimensional PCs plays an important role. The larger is the ratio, the wider is the total reflection band. From this point of view, the choice of the pair “Si-air” is very promising since such a pair possesses an extremely high contrast ratio (3.42/1 in a wide IR range). Structures with a great number of Si walls separated by air (so called grooved Si) can be obtained by vertical anisotropic etching of $\langle 110 \rangle$ Si in an alkaline solution through an oxide mask [2]. Fig. 1 shows the SEM image of a grooved Si structure developed by this method. To our best knowledge, the optical properties (reflection and transmission spectra) of this composite material in the middle infrared range were never studied before, despite the fact that Kendall [2] suggested their use as optical filters for the far-infrared region.

Furthermore, the position and the width of PBG can be tuned over a wide spectral range, the tuning being provided by varying the crystal lattice parameters and dielectric constants of materials composing PCs. In fact, the possibility to tune the PBG structure in real time is a challenging task [3]. It can be achieved by utilisation of substances with the ability to change their refractive index under external impact.

The high contrast ratio of grooved Si in the IR range, the presence of the smooth vertical walls and the possibility of the wide variety in the design and technology of such structures allow to suggest it as a matrix for the fabrication of a new composite

material, “grooved Si-LC”. The advantage of this structure is also in its simplicity which aids theoretical simulations and thus simplifies interpretation of experimental results. Therefore, the main objective of this study was fabrication, measurement and analysis of IR spectra obtained from matrixes and composite materials on the base of grooved Si.

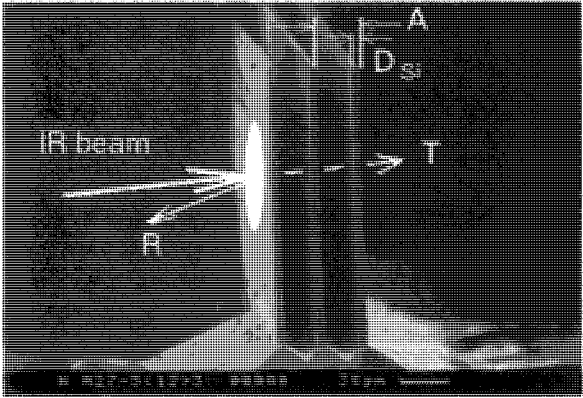


Figure 1. Schematic of FTIR measurements (R and T) on the periodic structure of grooved Si with lattice constant $A=24\text{ }\mu\text{m}$, width of Si wall $D_{Si}=2\text{ }\mu\text{m}$, and period number $m=3$.

2 Experimental

The best geometrical parameters of periodic Si structures were theoretically estimated before the structure preparation [4]. Using the procedure described elsewhere [5], the grooved Si samples were created: with lattice constant $A=16, 8,$ and $4\text{ }\mu\text{m}$, each sample with number of Si walls $m=50$ and the samples with $A=24, 12,$ and $10\text{ }\mu\text{m}$, $m=3$ and 4 . The lattice constant A may be written as: $A=D_{Si} + D_{Air}$. The Si structures were infiltrated by commercial nematic liquid crystal E7.

FTIR measurements in reflection mode in the range of $700\text{--}7000\text{ cm}^{-1}$ have been performed with a wavelength resolution of $0.001\text{--}0.05\text{ }\mu\text{m}$ using a Digilab FTS 6000 spectrometer in conjunction with a UMA 500 infrared microscope. IR measurements of grooved Si are critical to the direction of the light propagation through the whole structure [6,7]. All FTIR measurements were made with a polarizer placed before the microscope detector.

3 Reflection spectra of samples impregnated with liquid crystal

All the calculations have been performed using the matrix method [8]. The Si wall width, D_{Si} , and air interval, D_{Air} , were used as variable parameters. For the structure

with $A=4\text{ }\mu\text{m}$ the best fitting was obtained for $D_{\text{Si}}=1.2$ and $D_{\text{air}}=2.8\text{ }\mu\text{m}$ showing good agreement with the main maxima and minima (see Fig. 2). In accordance with calculations performed with these parameters, the main PBG lies in the range $\lambda=10\text{-}22\text{ }\mu\text{m}$ and can be partly identified (up to $\lambda=14\text{ }\mu\text{m}$) experimentally.

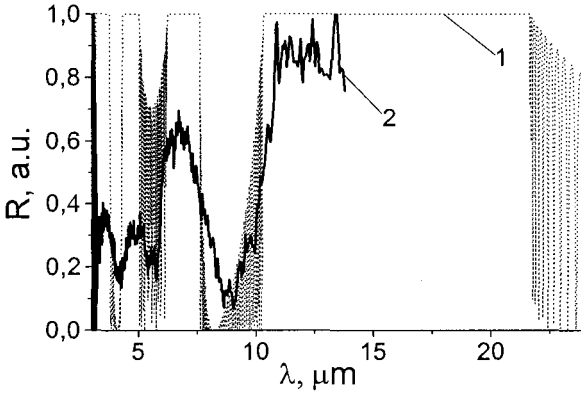


Figure 2. Calculated (1) and experimental (2) reflection spectra of empty grooved Si with lattice constant $A=4\text{ }\mu\text{m}$, $m=50$.

It should be noted that the agreement between the experimental and theoretical maxima and minima for most structures presented here and the good agreement between experimental spectra of reflection and transmission (Fig. 3) gives us the appropriateness of the chosen model and the high quality of the interfaces.

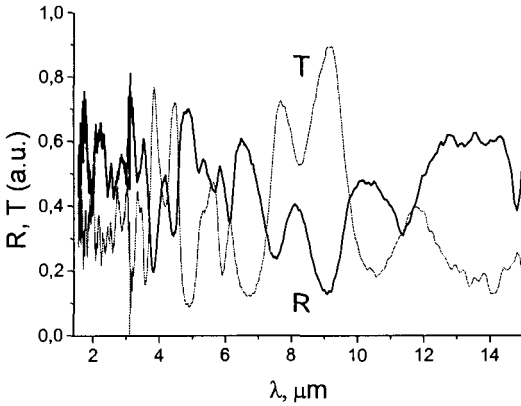


Figure 3. Experimental reflection and transmission spectra of empty sample with $A=10\text{ }\mu\text{m}$, $m=4$.

The reflection spectra of grooved Si samples with different lattice constants were investigated and the parameters of their periodical structures (D_{Si} and D_{air}) were determined. The latter was used for the analysis of the composites grooved Si+LC. The reflection spectra for some samples do not demonstrate an anisotropy, while for other samples the anisotropy shown in the spectra is quite substantial. We performed the fitting of the refractive index N_{LC} of LC filled in the grooves. This was done through a comparison of the experimental and calculated spectra for p - and s -polarized light, where N_{LC} was taken as a fitting parameter. Typically, the accuracy achieved was approximately $\Delta N_{\text{LC}}=0.01$. The values of N_{LC} calculated from the spectra for different polarisations are equal to 1.5 for p -polarisation and ranging from 1.5 to 1.65 for s -polarization. The calculations performed for spectra at s -polarization often do not fit well. This is possibly due to peculiarities of the optical properties of LC when impregnated. The obtained values of N_{LC} for p - and s -polarisations allow us to determine the orientation of LC in the grooves of the Si matrix.

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LARGE OPTICAL ANISOTROPY OF 1D PHOTONIC CRYSTAL FABRICATED BY VERTICAL ETCHING OF SILICON

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Periodic structures of deep narrow grooves with vertical walls were prepared by liquid anisotropic etching of silicon. It was shown experimentally that the obtained media possesses the properties of a negative uniaxial crystal with its optical axis lying in the wafer plane. These structures display a large optical anisotropy in the middle IR range of spectrum. The difference in the effective refractive indices of the ordinary and the extraordinary rays $\Delta n \approx 1.5$.

1 Introduction

The interest in optical properties of periodic structures, based on silicon, originates from the perspectives to use such structures as optical processing elements which can be implemented into the same chip with electronic devices. It is known that macroporous silicon with a regular pattern of deep channels forms two-dimensional (2D) photonic crystal (PC) [1]. Grooved silicon with the periodic "lattice" of Si ribs forms 1D PC [2,3].

Besides, both structures possess an optical anisotropy in the spectral range of $\lambda \gg a$ where a is the "lattice" constant. This is the so called anisotropy of shape described in [4]. Studies of birefringence in 2D PC from macroporous silicon [5] shows it is a positive uniaxial crystal with its optical axis oriented along the pores. The present work is focused on the studies of 1D PC from grooved Si. It is expected to be a negative uniaxial crystal whose axis is perpendicular to the Si ribs.

2 Experimental

To obtain the periodic structure of grooved Si we used chemical anisotropic etching of (110) Si wafer [6]. The narrow grooves, oriented precisely along the $\langle 111 \rangle$ crystallographic direction [7], formed an artificial lattice with periods $a = 4, 5$ and $6 \mu\text{m}$ for three samples under investigation (see Table). Si vertical ribs with thickness d_{si} of $\sim 1 \mu\text{m}$ are altered with air space of d_{air} thick. The depth of the

grooves $l = 30 \text{ }\mu\text{m}$. To enhance the durability of Si ribs their length was limited by $b=400 \text{ }\mu\text{m}$.

Optical characterization was performed by means of FTIR spectroscopy in the spectral range $450\text{-}6000 \text{ cm}^{-1}$ with resolution 8 cm^{-1} using Digilab FTS 60A spectrometer. The scheme of the experiment and the sample structure are shown in Fig. 1. Electric vector of the incidence light was oriented either parallel $E_{\parallel}$ or perpendicular $E_{\perp}$ with respect to the grooves. This corresponds to the propagation inside the crystal of the ordinary (o) and extraordinary (e) wave, respectively.

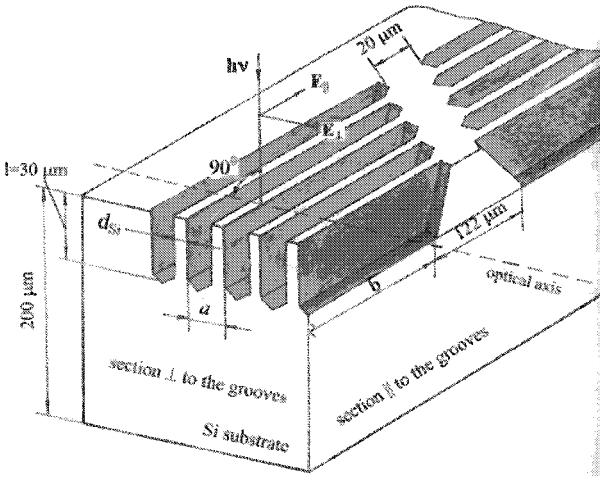


Figure 1. Structure of the samples and the scheme of optical measurements.

To find the anisotropy of the refractive indices Δn the classic optical geometry with a diagonal polarization of light was used. The incident light was polarized at 45° with respect to the optical axis of grooved Si sample as shown in Fig. 2. The analyzer A, situated after the sample, was oriented either parallel $A\parallel P$ or perpendicular $A \perp P$ to the polarizer.

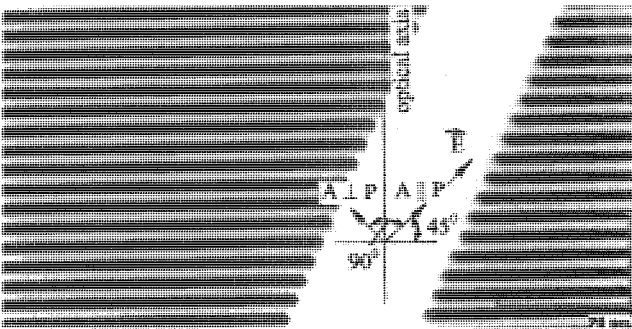


Figure 2. The top view of grooved Si sample and orientation of polarizer and analyzer with respect to the grooves under the measurements with diagonal polarisation.

3 Results and discussion

The reflection spectra of grooved Si sample with the lattice constant of 6 μm are shown in Fig. 3. These spectra differ significantly for two polarizations, $E_{\parallel}$ and $E_{\perp}$, manifesting that $n_e < n_o$. The effective refractive indices for ordinary and extraordinary waves were found from the neighboring extremes at ν_1 and ν_2

$$n_{o,e} = \frac{10^4}{4l(\nu_1 - \nu_2)}.$$

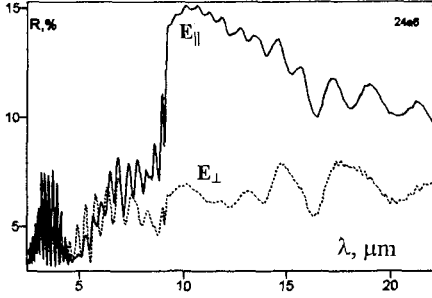


Figure 3. Reflection spectra of sample 24a6 for two different polarizations $E_{\parallel}$ and $E_{\perp}$ of incident light.

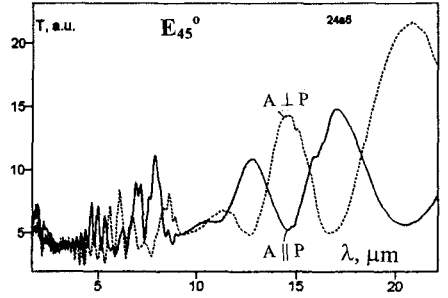


Figure 4. The transmission spectra of sample 24a6 for diagonal polarization geometry.

The transmission spectra of the same sample obtained in diagonal polarization geometry are shown in Fig. 4. The spectral position of the maxima for $A \perp P$ corresponds to the position of minima for $A \parallel P$. This is due to the phase shift of π for e and o waves at the exit from the grooved layer and enables to find

$$\Delta n = \frac{10^4}{2l(\nu_1 - \nu_2)}.$$

The values of n_o , n_e and Δn found for the samples with different

lattice constants are summarized in the Table. In this Table there are also calculated values obtained with the simple expressions for effective dielectric constants [4]:

$$\varepsilon_{\perp} = \frac{\varepsilon_1 \varepsilon_2}{f_1 \varepsilon_2 + f_2 \varepsilon_1} \text{ and } \varepsilon_{\parallel} = f_1 \varepsilon_1 + f_2 \varepsilon_2, \text{ where } f_1 = 1 - p = \frac{d_{\text{Si}}}{a}, f_2 = \frac{d_{\text{air}}}{a} = p \text{ and } \varepsilon_1,$$

ε_2 are dielectric constants for Si and air. Analysis of these formulas shows that our structures with high porosity $p = d_{\text{air}}/a = 0.75-0.77$ are not the best case to obtain the largest birefringence Δn . Although, they demonstrate high value $\Delta n \approx 1.5$, nearly independent from λ in the spectral range of $\lambda > 12 \mu\text{m}$. The experimental values of refractive indices n_o , n_e and anisotropy Δn are greater than the calculated data. The reason for this originates probably from the fact that the approximation $\lambda \gg a$ is not fulfilled. The infiltration of Si grooves with a nematic liquid crystal with an average refractive index $n_{\text{LC}} = 1.6$ have reduced Δn of the composite down to ≈ 1 in the qualitative agreement with the calculations.

Table. Geometric and optical parameters of grooved Si samples.

Sample №	a , μm	d_{Si} , μm	p	calculated			experimental			
				n_o	n_e	$n_o - n_e$	n_o	n_e	$n_o - n_e$	Δn
24a4	4	1	0.75	1.92	1.14	0.78	2.9	1.4	1.5	1.4
24a5	5	1.2	0.76	1.89	1.13	0.76	2.8	1.3	1.4	1.5
24a6	6	1.4	0.77	1.86	1.12	0.74	3.0	1.5	1.5	1.6
24a6(LC)	6	1.4		2.16	1.77	0.39	-	-	-	1.0

4 Conclusion

We developed and fabricated an artificial uniaxial crystal and found its birefringence in the middle IR spectral range. The effective Δn of about 1.5 is greater than birefringence of macroporous silicon ($\Delta n = 0.366$) [5] and much greater than birefringence of the well known natural crystal CaCO_3 ($\Delta n = 0.172$). An important advantage of the grooved Si, contrary to the macroporous Si, is the in-plane position of its optical axis. A proper choice of the grooved Si porosity ($p = 0.325$) should increase Δn even more.

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STRAIN-INDUCED SELF ASSEMBLING OF NANOVoids IN Si/SiGe MULTI-LAYER STRUCTURES

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We report on self-assembled formation of spherically shaped voids in MBE grown SiGe alloy layers implanted *in-situ* at elevated temperature with low-energy Ge ions, followed by thermal annealing. The voids are of nanometer size and are exclusively assembled in thin SiGe quantum wells. The voids only appear in the layers after heat treatment at a temperature higher than 700 °C, and they are stable up to 950 °C. The results are discussed in terms of the separation of the vacancies and interstitials induced by the strain situation around the SiGe quantum wells.

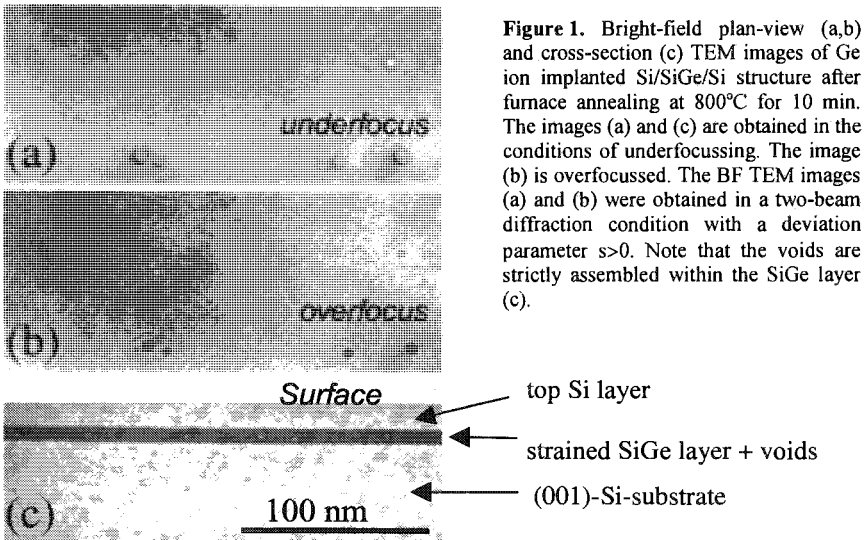
Nanometer sized voids introduced in Si and SiGe alloys are of significant interest due to a number of promising applications such as light emission from localized defect regions, gettering of metallic impurities in integrated circuits, and layer splitting for Smart-Cut technology [1-4]. The typical way of void formation is implantation of hydrogen or helium ions followed by thermal treatment. The interaction of the imbedded impurity atoms with the vacancies results in generation and growth of the voids. In this case, the voids are broadly distributed in both space and size, which reflect the depth distribution of the implants and created defects, the high-temperature conditions of diffusion and the Oswald ripening process [1,4].

In the present paper we demonstrate the formation of an array of precisely self-adjusted nano-voids. The nano-voids are obtained as a result of implantation of Ge ions followed by a thermal treatment. The means of self-ordering of the voids utilizes the strain situation around thin SiGe layers (quantum wells) incorporated into a thick Si layer [5]. Due to compressive strain, SiGe/Si layers may effectively getter and accumulate vacancies and vacancy-related defects, which transform into nanovoids during subsequent thermal treatment.

The samples were grown by solid-source MBE using e-beam evaporators for the Si and Ge deposition and a build-in low energy (1 keV) ion implanter. Wafers of p-type (001) Si were used as substrates. Following the SiO₂ desorption from the surface at 850 °C, a 100 nm-thick Si buffer layer was grown. Subsequently, a buffer structure was grown at 525 °C consisting of four alternating layers of 3 nm Si and 2.8 nm Si_{0.5}Ge_{0.5}. Typical growth rates were 0.084 Å/s and 0.1 Å/s for the Si and Si_{0.5}Ge_{0.5} layers, respectively. During the growth of this four-layered buffer structure, Ge⁺ was implanted *in situ* at a current density of 0.02 μA/cm² to a total dose of about 1.6x10¹⁴ cm⁻². Finally, a 10 nm Si cap layer was deposited. The wafers were annealed at temperatures between 600 and 950 °C in a furnace for 10 min or by 30 s rapid thermal annealing (RTA) in N₂ or O₂ ambiances. The layer

structures were investigated by transmission electron microscopy (TEM) in both plan-view (PVTEM) and cross-section (XTEM) modes, using a Philips CM20 instrument operating at 200 kV. The TEM specimens were thinned down to electron transparency using a procedure consisting of successive mechanical polishing and ion-beam milling.

It is observed by TEM [5] that the as-implanted Si/SiGe/Si samples contain clusters of point defects and extended planar defects along the (001) and (111) planes (not shown). Annealing above $\sim 750\text{ }^{\circ}\text{C}$ results in an abnormal structural transformation: a large density ($10^9 - 5 \times 10^{10}\text{ cm}^{-2}$) of circular defects, but no dislocation loops, are found in the layers. Figures 1 (a) and (b) show a matched pair of two-beam, bright-field, under- and overfocused TEM micrographs obtained from a thin film in a two-beam diffraction condition with a deviation parameter $s > 0$. The defects show minimal contrast at focus. In the underfocused micrograph (Fig. 1(a)) the defects are imaged as bright circles surrounded by Fresnel fringes, whereas in the overfocused micrograph (Fig. 1(b)) they display a dark contrast. In the “out-of-Bragg conditions”, they keep their circular shape after large inclinations of the sample in the microscope with respect to the electron beam, and they do the same in the cross-section view (Fig. 1(c)). In accordance with Ref. [6], the above observations demonstrate that the circular defects are open-volume defects or voids. Please note, that the voids are solely located within the layer of SiGe (Fig. 1 (c)).



There are several indications that the voids originate from, and develop by means of the evolution of, vacancies and (or) V -related defects [5]. First, the voids increase in size and decrease in density with increasing temperature. However, the

total volume occupied by the voids (C_v) remains constant around $C_v = 5 \times 10^{-9} \text{ cm}^3/\text{cm}^2 \pm 20\%$. Similar to Ref. [4] we believe that the temperature and time evolution of the voids can be explained as a conservative Ostwald ripening process which involves vacancy (V) diffusion from small voids to larger ones.

Second, it is found from a comparative study of the samples annealed in oxygen or in nitrogen ambiances that oxidation of Si results in a reduced value of C_v and in a more homogeneous size distribution of the voids. These results indicate that the vacancies, emitted by the small voids, more likely annihilate with the oxidation-induced self-interstitials and, therefore, do not reach and attach to the large voids. Finally, there is a correlation between the number of vacancies N_v in the voids and the number of implanted dopant atoms. The vacancies created during implantation can be partially trapped and accumulated within the SiGe layer due to the compressive strain.

Fig. 2 presents the structures of the samples implanted with Ge and annealed in the temperature range of 600-750 °C. Compared to the as-grown sample, only insignificant modifications of the size, shape and density of implantation induced defects take place during annealing at 600 °C (Figs. 2(a)). A further increase of the temperature to 650 °C, however, results in significant growth of the largest point defect clusters at the expense of the smallest followed by defect coalescence into some kind of defect ensembles (Fig. 2(b)). The next important stage is a threshold-like transformation of clusters of point defects to the voids, which happens in the temperature range between 700 and 750 °C (Figs. 2(c) and

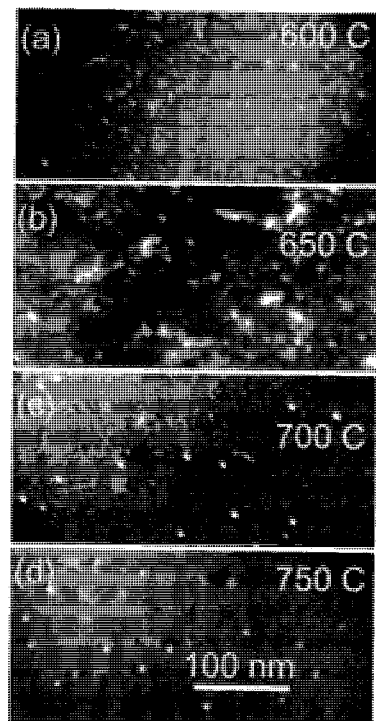


Figure 2. Dark-field weak beam TEM images of Si/SiGe/Si structures which were *in-situ* implanted with Ge and furnace annealed at 600 °C (a), 650 °C (b), 700 °C (c) or 750 °C (d) for 10 min in a dry N_2 [5]. Note that the main nucleation of voids and annealing of as-implanted defects take place in the temperature range 650-750 °C.

(d)). The nucleation and growth of the voids is accompanied by the disappearance of the point defect clusters: both voids (bright spots of 5-7 nm large) and point defect clusters (fine granular background with a typical grain-size of about 1-3 nm in the TEM picture) simultaneously exist in the dark-field weak-beam TEM image in this case (Fig. 2(c)). A further increase of the temperature to 750 °C results in a slight increase of the size/density of the voids and annealing of the point defect clusters.

A mechanism based on spatial separation of Frenkel pairs has been discussed to account for the observed selection of vacancies and interstitials [7] and the vacancy excess within the region around $R_p/2$. The mechanism seems to have reasons in the case of MeV implanted samples, where the I and V peak concentrations are well separated in the space with a reduced $I - V$ annihilation probability. In the present work, however, Ge ions were implanted at elevated temperature and at an energy as low as 1 keV which prevent the kinematic spatial separation of V and I . An explanation of the fact that the voids assemble within the SiGe layer, as it can be well recognized from the XTEM image in Fig. 1(c), must be sought in the strain situation of the SiGe layer. The SiGe layer is compressively strained after growth and before annealing and there is no indication that the layer has relaxed during the subsequent annealing. Thus, the assembly of the voids in the strained SiGe layer could be a strain-relieving phenomenon; similar effect has previously been demonstrated in strained SiGe layers in which hydrogen-related voids partly relieve the strain [8]. We believe that at the first stage *strain-induced (enhanced)* indiffusion of the vacancies and their accumulation within the layer of SiGe takes place. This is then followed by void nucleation and growth at high annealing temperature.

In conclusion, spherically shaped nanovoids are produced in MBE grown SiGe alloy layers with *in-situ* implantation of low-energy Ge ions followed by thermal treatment at temperatures above $\sim 750^\circ\text{C}$; the nanovoids grow in size with increasing anneal temperature and are stable up to 950°C .

Acknowledgement

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OPTICAL DIAGNOSTICS OF NANOMETER DIELECTRIC FILMS BY COMBINING ELLIPSOMETRY AND DIFFERENTIAL REFLECTANCE

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The effect of nanometer dielectric films on the ellipsometric parameters and reflectance of linearly polarized light is investigated within the framework of the perturbation theory. The novel approach is developed for simultaneous determining the thickness and dielectric constant of nanometer-scale films by the differential reflectance and ellipsometric measurements.

1 Introduction

Optical methods, particularly, ellipsometry and various photometric techniques, are successfully employed for a long time in investigation of thin films because they are fast, inexpensive, and noninvasive. At present, the diagnostics of ultrathin films is attracting an increased level of interest, especially in modern materials technology [1]. In the case of nanometer films, it is best to apply the differential methods [2,3], which are based on the direct measurement of the ultrathin film contribution to the reflectance and ellipsometric parameters. The use of exact equations with numerical techniques for determining the parameters of nanometer-scale layers from reflection characteristics is rather complicated because of the high-order nonlinear equations have many physically meaningful solutions. However, the mathematical relationships take a relatively simple form in the long-wave limit, which is very useful for the inverse problem solution.

The purpose of this paper is to study the differential ellipsometric and reflectance characteristics of an ultrathin dielectric film in the long-wave limit and to take a further look for determining the parameters of nanoscale films on the basis of first- and second-order approximate expressions for reflection characteristics.

2 Absorbing substrate

We consider the reflection of s- and p-polarized time-harmonic electromagnetic plane wave in an ambient medium of real dielectric constant ε_a from a plane-parallel layer medium consisting of a semi-infinite absorbing substrate with dielectric constant $\hat{\varepsilon}_s = \varepsilon_s + i\xi_s$ and an ultrathin dielectric film with thickness $d_1 \ll \lambda$ and real dielectric constant ε_1 . We assume that all media are uniform, isotropic and nonmagnetic. Ultrathin dielectric layers are considered

phenomenologically within the scope of macroscopic electrodynamics by using the concept of local dielectric constant.

Let us calculate the small contributions of nanometer layers to ellipsometric parameters. In long-wavelength approximation in the first order with respect to the small parameter d_1/λ for $\partial\Psi = \Psi - \Psi_0$ and $\delta\Delta = \Delta - \Delta_0$, where Ψ, Δ and Ψ_0, Δ_0 are the ellipsometric angles of an ultrathin film and a bare substrate ($d_1 = 0$), respectively, we obtain the following approximate formulas:

$$\partial\Psi \approx 2\pi\varepsilon_a^{1/2}\xi_s \cos\varphi_a \sin^2\varphi_a \sin 2\Psi_0 A_1^{-1}(\varepsilon_1 - \varepsilon_a)\varepsilon_1^{-1}(a_2 M_1 - a_1 M_2)(d_1/\lambda), \quad (1)$$

$$\delta\Delta \approx 4\pi\varepsilon_a^{1/2} \cos\varphi_a \sin^2\varphi_a A_1^{-1}(\varepsilon_1 - \varepsilon_a)\varepsilon_1^{-1}(a_1 M_1 + \xi_s^2 a_2 M_2)(d_1/\lambda), \quad (2)$$

$$A_1 = M_1^2 + \xi_s^2 M_2^2, \quad a_1 = \varepsilon_s \varepsilon_1 + \xi_s^2 - \varepsilon_s^2, \quad a_2 = 2\varepsilon_s - \varepsilon_1,$$

$$M_1 = \varepsilon_a \varepsilon_s - \varepsilon_a^2 \sin^2\varphi_a + (\xi_s^2 - \varepsilon_s^2) \cos^2\varphi_a, \quad M_2 = 2\varepsilon_s \cos^2\varphi_a - \varepsilon_a,$$

The expression (2) gives exactly the same values for $\delta\Delta$ as the previously derived formula [4]. However, the expression for $\partial\Psi$ quoted in the literature [4,5] is in error. Furthermore, the employment of that formula for the case, where $\xi_s \ll \varepsilon_s$ and ξ_s is not much greater than d_1/λ , is incorrect for example, if $\varphi_a = 45^\circ$, $\varepsilon_a = 1$, $\varepsilon_1 = 2.25$ and $\varepsilon_s^{1/2} = 4 + i0.5$, then the relative errors for $\partial\Psi$ of approximate expression (6) of paper [4] and the presented formula (1) are -873.4% and 2.919% for $d_1/\lambda = 10^{-3}$ and -902.4% and 0.0303% for $d_1/\lambda = 10^{-5}$, respectively.

Next, we examine the possibilities of determining the dielectric constant of nanometer films by using the pure ellipsometric method or the combination of ellipsometric and reflectivity measurements. In the case of ellipsometry a convenient quantity is ratio $\partial\Psi/\delta\Delta$ (or vice versa). On condition that $\delta\Delta$ and $\partial\Psi$ are measured at the same angle of incidence φ_a from Eqs. (1) and (2) we obtain

$$\varepsilon_1 \approx (2\varepsilon_s f_1 + \varepsilon_s^2 - \xi_s^2)/(f_1 + \varepsilon_s), \quad (3)$$

$$f_1 = [M_1 - 2M_2 \xi_s (\sin 2\Psi_0)^{-1}(\partial\Psi/\delta\Delta)]/[M_2 + 2M_1 (\xi_s \sin 2\Psi_0)^{-1}(\partial\Psi/\delta\Delta)].$$

Similar unambiguous expressions for ε_1 can be obtained by combining the changes in the ellipsometric angles and the differential reflectance of s- or p-polarized light, i.e., the ratios $\delta\Delta/(\Delta R_1/R_0)^{(p,s)}$ or $\partial\Psi/(\Delta R_1/R_0)^{(p,s)}$. It must be emphasized that the differential reflectance is an immediately measurable quantity because the relative change in the intensity of the reflected signal

$$\Delta I_1^{(R)}/I_0^{(R)} = (I_1^{(R)} - I_0^{(R)})/I_0^{(R)} = (R_1^{(p,s)} I^{(i)} - R_0^{(p,s)} I^{(i)})/(R_0^{(p,s)} I^{(i)}) = \Delta R_1^{(p,s)}/R_0^{(p,s)},$$

where $I_1^{(R)}$ and $I_0^{(R)}$ are the reflected intensities from nanometer film and bare substrate, respectively, and $I^{(i)}$ is the intensity of the incident light.

Since at oblique angles $(\Delta R_1 / R_0)^{(p)} \gg (\Delta R_1 / R_0)^{(s)}$, p-polarized light can be used more successfully in practice. Using Eqs. (1), (2), and Eq. (1) for $(\Delta R_1 / R_0)^{(p)}$ from paper [2], we obtain the following approximate formulas:

$$\varepsilon_1 \approx [M_1(\varepsilon_s^2 - \xi_s^2) - 2M_2\varepsilon_s\xi_s^2 + f_2\varepsilon_a] / [M_1\varepsilon_s - M_2\xi_s^2 + f_2ctg^2\varphi_a], \quad (4)$$

$$\varepsilon_i \approx [2M_1\varepsilon_s + M_2(\varepsilon_s^2 - \xi_s^2) - f_3\varepsilon_a] / [M_1 + M_2\varepsilon_s - f_3ctg^2\varphi_a], \quad (5)$$

$$f_2 = 2\xi_s K A_1 [\delta\Delta / (\Delta R_1 / R_0)^{(p)}],$$

$$f_3 = 4K A_1 (\sin 2\Psi_0)^{-1} [\partial\Psi / (\Delta R_1 / R_0)^{(p)}],$$

$$K = [1 - 2\varepsilon_a\varepsilon_s(\varepsilon_s^2 + \xi_s^2)^{-1} \sin^2 \varphi_a] [\{\varepsilon_a(1 - \varepsilon_a\varepsilon_s(\varepsilon_s^2 + \xi_s^2)^{-1} \sin^2 \varphi_a) - \varepsilon_s \cos^2 \varphi_a\}^2 + \xi_s^2 \{\cos^2 \varphi_a - \varepsilon_a^2(\varepsilon_s^2 + \xi_s^2)^{-1} \sin^2 \varphi_a\}^2]^{-1},$$

if differential reflectance and ellipsometric quantities are determined at the same incident angle φ_a . Note that the use of reflectance in combination with ellipsometry for optical diagnostics has been proposed a long time ago [6]. However, only numerical techniques, which suffer from significant shortcomings, were employed for the inverse problem in these analyses.

3 Transparent substrate

Let us consider the effect of dielectric nanometer film on the ellipsometric angles and on the reflectance of linearly polarized light from transparent substrate ($\xi_s \equiv 0$). For the contributions of an ultrathin layer to ellipsometric angles we obtain the following approximate formulas:

$$\delta\Delta \approx 4\pi\varepsilon_a^{1/2} \cos\varphi_a \sin^2 \varphi_a (\varepsilon_s \cos^2 \varphi_a - \varepsilon_a \cos^2 \varphi_s)^{-1} (\varepsilon_a + \varepsilon_s - \varepsilon_1 - \varepsilon_a\varepsilon_s\varepsilon_1^{-1})(d_1 / \lambda), \quad (6)$$

if $\varphi_a \neq \varphi_B$ (for $\varphi_a = \varphi_B$, we have $\delta\Delta = \pi / 2$), and

$$\partial\Psi \approx \pi(\varepsilon_a + \varepsilon_s)^{1/2} (\varepsilon_s - \varepsilon_a)^{-1} (\varepsilon_a + \varepsilon_s - \varepsilon_1 - \varepsilon_a\varepsilon_s\varepsilon_1^{-1})(d_1 / \lambda), \quad (7)$$

if $\varphi_a = \varphi_B$ (for $\varphi_a \neq \varphi_B$ $\partial\Psi \sim (d_1 / \lambda)^2$, and the corresponding expression is very cumbersome and lacks practicality).

In the absence of absorption the contribution of nanometer layer to the reflectance in the first order in small parameter d_1 / λ is equal to zero. Therefore, the differential reflectance must be expressed at least in the second order with respect to d_1 / λ . For example, in the case of s-polarization

$$(\Delta R_1^{(s)} / R_0^{(s)}) \approx 16\pi^2 n_a n_s \cos\varphi_a \cos\varphi_s (\varepsilon_a - \varepsilon_s)^{-2} [(\varepsilon_a - \varepsilon_1)(\varepsilon_s - \varepsilon_1)](d_1 / \lambda)^2. \quad (8)$$

Next, in the case of transparent substrate the pure ellipsometric method is not applicable for the determination of ε_i on the basis of approximate Eqs. (6) and (7) whereas the relation $\delta\Delta/\partial\Psi$ is independent of ε_i . If ellipsometric parameter $\delta\Delta$ is measured at $\varphi_a = \varphi_a^{(e)}$ and differential reflectance $(\Delta R_1/R_0)^{(0)}$ at $\varphi_a = 0$ then from Eqs. (6) and (8) we obtain

$$\begin{aligned} & (\delta\Delta)^2 / (\Delta R_1/R_0)^{(0)} \approx n_a n_s^{-1} \cos^2 \varphi_a^{(e)} \sin^4 \varphi_a^{(e)} (\varepsilon_s - \varepsilon_a)^2 \\ & \times (\varepsilon_s \cos^2 \varphi_a^{(e)} - \varepsilon_a \cos^2 \varphi_a^{(e)})^{-2} (\varepsilon_1 - \varepsilon_a)(\varepsilon_1 - \varepsilon_s) \varepsilon_1^{-2}. \end{aligned} \quad (9)$$

Under condition $\varepsilon_1 > \varepsilon_a$ or $\varepsilon_1 > \varepsilon_s$ the expression $(\varepsilon_1 - \varepsilon_a)(\varepsilon_1 - \varepsilon_s) \varepsilon_1^{-2}$ has identical value for two different values of ε_1 which are related by the relation $\varepsilon_1^{(2)} = \varepsilon_1^{(1)} \varepsilon_{as} / (\varepsilon_1^{(1)} - \varepsilon_{as})$. Hence, it is obvious that the solution of the inverse problem, i.e., the determination of ε_i from $(\delta\Delta)^2 / (\Delta R_1/R_0)^{(0)}$, is generally not unique; there are two physically meaningful solutions:

$$\varepsilon_1 \approx (\varepsilon_s + \varepsilon_a \pm [(\varepsilon_s - \varepsilon_a)^2 + 4\varepsilon_a \varepsilon_s t]^{1/2}) / (2[1 - t])^{-1}, \quad (10)$$

$$t \equiv \frac{n_s (\varepsilon_s \cos^2 \varphi_a^{(e)} - \varepsilon_a \cos^2 \varphi_a^{(e)})^2}{n_a \cos^2 \varphi_a^{(e)} \sin^4 \varphi_a^{(e)} (\varepsilon_s - \varepsilon_a)^2} \frac{(\delta\Delta)^2}{(\Delta R_1/R_0)^{(0)}}. \quad (11)$$

The false solution of Eq. (10) can be recognized from the following circumstances. For $\varepsilon_1 > \varepsilon_a$ the quantity $\Delta R_1^{(p,s)}(\varphi_a = 0) \equiv \Delta R_1^{(0)} > 0$ if $\varepsilon_1 > \varepsilon_s$ and $\Delta R_1^{(0)} < 0$ in the opposite situation. If both solutions of Eq. (10) are greater (less) than ε_s , then the correct value of ε_i can be selected on the basis of the fact that the angular dependence of $\Delta R_1^{(p)}(\varphi_a)$ changes sign near the angle $\varphi_a = \arctan(n_1/n_a)$.

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PHOTONIC AND NONLINEAR-OPTICAL MEDIA BASED ON NANOSTRUCTURED SEMICONDUCTORS

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Structures made by electrochemical nanostructuring of semiconductors show photonic band gap tunable with the period of structure, nanostructure sizes and their dielectric surroundings. Experiments demonstrate both phase matching for second-harmonic generation and an enhancement of second- and third-harmonic generation efficiencies in the nanostructured materials.

1 Introduction

Nanostructuring of semiconductors and dielectrics is a promising way for fabricating new photonic and nonlinear optical media [1-3]. Electrochemically prepared porous silicon (PS) consists of nanostructures and voids with dimensions varied from 1-2 to 200 nm. 1D and 2D photonic crystals as well as birefringent media can be easily formed on the base of PS by choosing size, shape and spatial orientation of nanostructures [2,3]. Multilayer structures of PS show 1D photonic band gap (PBG) tunable with the period of structure, sizes of Si nanocrystals and their dielectric surroundings. PS layers produced by anisotropic electrochemical etching of c-Si (110) exhibit strong in-plane birefringence [4]. The films of macroporous PS possess properties of a positive uniaxial crystal having the optical axis along the pores [5]. Experiments demonstrate possibility to reach phase matching for second-harmonic generation in PS multilayers and birefringent films [6-8].

2 Results and discussion

Fig. 1 shows an example of reflection spectra for the multilayer structure formed from p^{++} -Si (110) substrate consisting of 12 pairs of alternating layers having porosities of about 60 and 70%, and mean refractive indices $\langle n_1 \rangle = 2.40$ and $\langle n_2 \rangle = 1.65$, correspondingly. The thicknesses of the low- and high-porosity layers are $d_1 = 70$ nm and $d_2 = 100$ nm, respectively. Because of the in-plane birefringence of (110) PS the structure acts as a polarization-sensitive Bragg reflector. The difference in wavelengths $\Delta\lambda_{ph}$ between the PBG for light polarized along and perpendicular to the optical axis is about 70 nm that is in agreement with a simple estimation $\Delta\lambda_{ph} = 2\Delta n(d_1 + d_2)$, where $\Delta n = 0.2$ is the mean value of birefringence. The

large difference in PBG for different polarization has prospects to be used in fabricating photonic components like dichroic mirrors, filters, “planar Brewster” windows, etc.

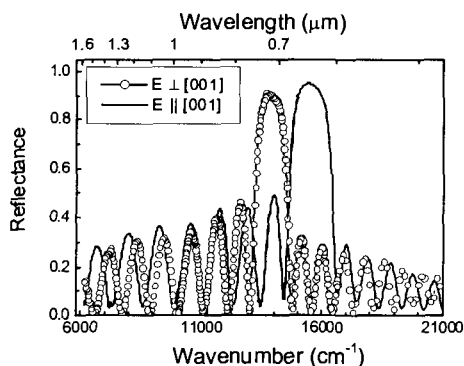


Figure 1. Reflection spectra of a multilayer formed on $p^{++}\text{-Si}$ (110). Measurements were done for light polarized along or perpendicular to the [001] crystallographic direction.

Experiments on second harmonic (SH) generation have revealed phase matching conditions for wave interaction in the birefringent PS layers. Fig. 2 demonstrates the dependence of SH intensity versus angle of incidence. The SH was measured in transmission geometry by using a Nd-YAG laser (1063 nm, 20 ps) as a pump source. For the PS film with air-filled pores the maximal SH intensity is observed at the angle of incidence of about 57° , whereas it is reached at 38° , when the pores are filled with ethanol, and 32° , when the pores are filled with glycerol. The change in the angle of the maximal SH signal is explained by the variation of the phase-matching condition caused by filling the pores with dielectric medium. In fact, the refractive index of glycerol (1.47) is larger than that for ethanol (1.36) and air. According to our calculations of the phase mismatch this leads to the change of the angle of phase matching due to dielectric tuning of the birefringence value of the PS. For the cases of ethanol- and glycerol-filled pores, the SH generation efficiency is several orders of magnitude higher than for the sample in air that is indicative of phase-matched SH generation.

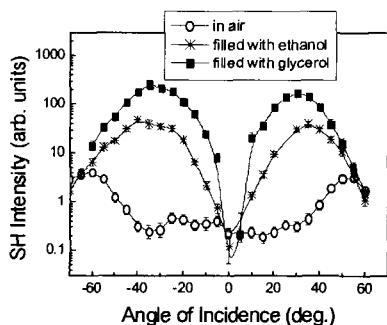


Figure 2. Angular dependence of second-harmonic intensity for a (110) PS film with the air-, ethanol-, and glycerol-filled pores.

The experiments on second- and third-harmonic generation in the reflection geometry demonstrate a giant enhancement of nonlinearities of the birefringent PS films. The effect cannot be explained in terms of effective medium approximation and is apparently related to strong local fields in nanostructured solids (Fig. 3).

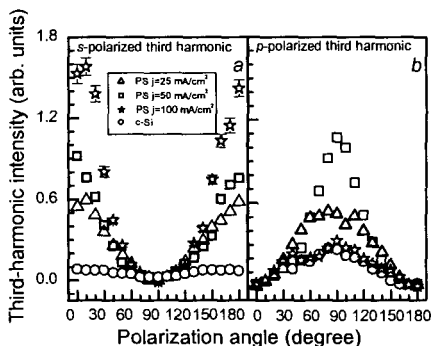


Figure 3. Polarization dependences of the third-harmonic intensity for the PS layers of different porosities grown on p^{++} -Si substrate as well as the c-Si: (a) s -polarized third harmonic and (b) p -polarized third harmonic.

Thus, the electrochemically nanostructured silicon is shown to be promising material for photonics and nonlinear optics. The strong in-plane birefringence of PS layers produced from (110) p^{++} -Si substrates allows us to control the efficiency of SH generation. The birefringence is tunable by changing the porosity and/or dielectric properties of material embedded in the pores. Furthermore, the PBG and/or birefringent PS can serve as phase-matching matrices for optically nonlinear substances incorporated in their pores that expands significantly the choice of nonlinear optical materials.

Acknowledgements

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OPTICAL PROPERTIES OF MULTILAYER HETEROSTRUCTURES BASED ON ZnSe/ZnS

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Growth of multilayer periodic ZnS/ZnSe heterostructures by metalorganic chemical vapor deposition, their optical properties examined by ellipsometry and traditional spectroscopy are described. The results obtained evidence that the structures proposed are promising as efficient Bragg reflectors for blue semiconductor lasers. Reflection coefficient higher than 90% in the blue-green spectral range have been obtained.

1 Introduction

Modern design of efficient surface emitting semiconductor lasers implies monolithic solid state structures with an active layer and periodic multilayer stacks comprising Distributed Bragg Reflectors (DBR). The latter provides reflection band at the emission wavelength due to multiple reflection/interference in a complex medium with periodically graded refraction index of the layers [1]. The larger is the refraction index difference $\Delta n = |n_1 - n_2|$ between a couple of materials chosen to develop a DBR and their average n value with respect to an ambient medium n_0 , the higher is the reflection coefficient for a given number of periods in a structure. For a given n_0 , n_1 , and n_2 reflection grows up with the number of periods in a structure. Therefore, engineering and development of DBR for semiconductor lasers is a trade-off between technological compatibility, lattice matching and refraction index contrast of materials involved.

The problem is solved successfully for III-V compounds emitting in the near infrared spectral range were a unique pair of GaAs – AlAs (difference of the refraction index $\Delta n \approx 0.7$, mismatch of a crystal lattice constant $\Delta a \approx 0.0016$) is applicable. Recent advances in efficient light emitting structures based on ZnSe require development of spectrally and technologically compatible high quality DBR-components. The structures under consideration are ZnMgSe/ZnCdSe structures fabricated by molecular beam epitaxy (MBE) [2], ZnMgSe/ZnSeTe MBE-structures [3], and MOCVD ZnMgSSe/ZnSSe structures [4]. For all structures

the reflection coefficients obtained were low enough for practical application in laser design. In the present contribution, we report on fabrication and optical properties of periodic ZnSe/ZnS heterostructures which are considered as a promising DBR-solution for blue lasers based on II-VI compounds.

2 Results and discussion

ZnS/ZnSe hererostructures were grown by metallorganic chemical vapor deposition (MOCVD) technique. The growth was performed in $\text{Zn}(\text{C}_2\text{H}_5)_2\text{-(CH}_3)_2\text{Se-(C}_2\text{H}_5)_2\text{S}$ system under hydrogen pressure close to atmospheric one in a home made quartz reactor ($T = 425\text{-}470^\circ\text{C}$). GaAs single crystal substrates with (100) orientation have been used. Optical constants of single ZnS and ZnSe layers and heterostructures were evaluated by means of spectral ellipsometry with binary modulation of polarization state. Growth and ellipsometry details have been described elsewhere [5]. Parameters of periodic heterostructures were chosen to get optical reflection maximum in the blue range. Samples square was approximately 0.5 cm^2 .

Optical properties of single crystal samples of ZnSe and ZnS are shown in Fig. 1. Good agreement of experimental and calculated spectra have been obtained using a model which includes not only GaAs substrate and ZnSe single crystal layer but a thin oxide layer on top of the ZnSe film. This surface layer was estimated to have thickness in the range of 3 to 8 nm, its optical constants being $n = 1.5\text{-}1.7$ and $k = 0.02\text{-}0.1$ within the spectral range investigated. Well pronounced excitonic features in ZnSe films near 450 nm evaluated at room temperature by ellipsometry prove high quality of the films. The results also prove the expected difference in refraction indexes of ZnSe and ZnS films to be 0.3-0.35 in the spectral range from 470 to 500 nm.

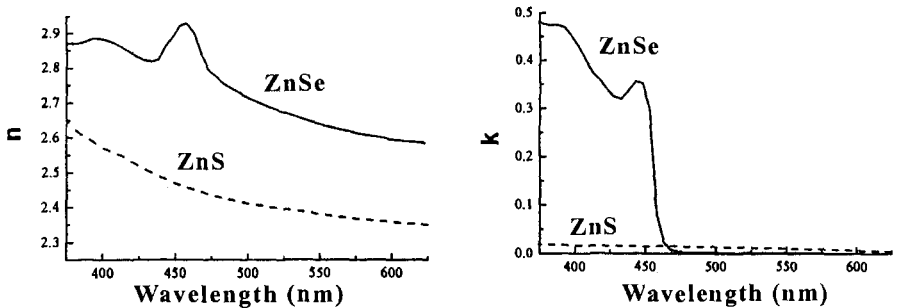


Figure 1. Spectral dependence of refractive (left) and absorption (right) indexes of single crystal ZnSe and ZnS films fabricated on a GaAs substrate by MOCVD process.

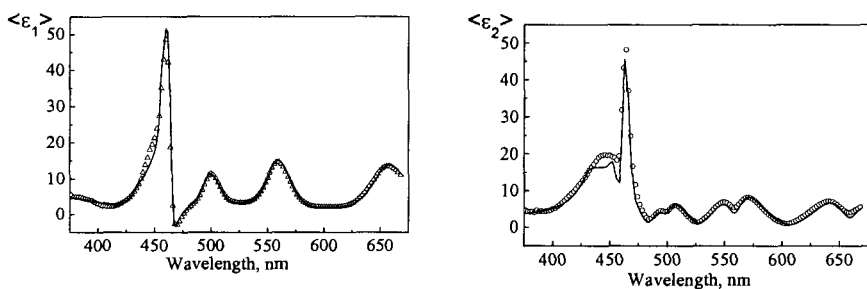


Figure 2. The spectra of real $\langle \epsilon_1 \rangle$ (left) and imaginary $\langle \epsilon_2 \rangle$ (right) parts of the pseudodielectric function $\langle \epsilon \rangle = \langle \epsilon_1 \rangle + i\langle \epsilon_2 \rangle$ for the multilayer structure. Circles and triangles – experimental data; straight line – calculated spectra.

Fig. 2 presents experimental and theoretical data for real and imaginary parts of the pseudodielectric function of a multilayer structure with the following parameters: GaAs substrate / 271 nm ZnSe / five pairs of layers (42 nm ZnSe / 45 nm ZnS) / 5 nm-thick surface overlayer. Sharp spectral peculiarities in the range near 460 nm coincide with the energy of exciton resonance and therefore provide a reliable prove of perfect crystalline structure remaining in multilayer stacks.

As one can see in Fig. 3, reflectivity of 12-layers structure is about 90%. Structures with a larger number of layers were found to exhibit even higher reflectivity. The maximal reflectivity up to 99% was obtained for a 20-layers DBR-structure on a GaAs substrate which is the uppermost value reported to date for the blue range for DBR semiconductor structures [6].

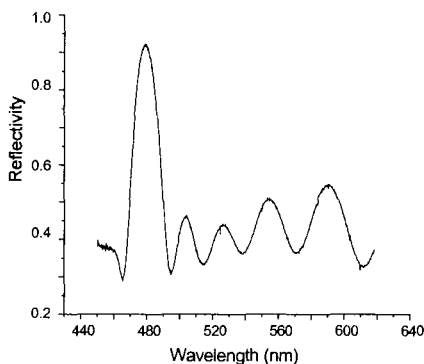


Figure 3. Optical reflection spectrum of a 12-layers ZnSe/ZnS heterostructure fabricated on a GaAs substrate.

Notably, pronounced excitonic features inherent in ZnSe single crystals remain in DBR-structures. This makes possible to use strong excitonic optical nonlinearities which are known for ZnSe single crystal [7] to get nonlinear DBR-structures with

optically tunable reflection/transmission spectra. Nonlinear properties of ZnS/ZnSe periodic nanostructures will be the subject of forthcoming experiments.

3 Conclusion

MOCVD growth of ZnS/ZnSe multilayer periodic heterostructures has been reported and their properties examined by ellipsometry and traditional spectroscopy are discussed. The results evidence high optical quality of the films which is proved by pronounced excitonic features. Distributed Bragg reflectors based on the grown structures are promising for semiconductor surface emitting lasers operating in the blue range.

Acknowledgements

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CONFINED OPTICAL VIBRATIONS IN ZnSe QUANTUM DOTS

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Highly monodisperse ZnSe nanocrystallites (NCs) were deposited on free-standing porous silicon. Optical phonons confined in nearly spherical ZnSe QDs have been studied theoretically and experimentally. Spatially quantized phonon modes are considered in the framework of the continuum model. Raman scattering and absorption of far-infrared (FIR) radiation in ZnSe quantum dots have been studied. Experimental FTIR transmittance spectra of porous silicon free layers containing nearly spherical ZnSe nanocrystals show a broad band between the bulk TO and LO phonon frequencies.

1 Introduction

Recent years several advanced technologies permit the growth of semiconductor NCs with quasi-zero-dimensional properties. The diameter of these NCs is in the range of few nanometers. Novel physical properties appear which suggest a broad range of device applications.

While the electronic and optical properties of semiconductor NCs are well understood, the vibrational properties (phonons confined in spherical quantum dots of several nanometers in size) of NCs received much less attention until the last few years [1-4]. An accurate description of the vibrational modes of a NC is of fundamental interest and is required to understand the coupling of vibrational modes to electronic charge. Recently, it has been shown theoretically that geometrical confinement becomes important both for infrared and Raman-active phonons in the limit of a small size of QDs [5]. In this paper, we report the observation of coupled phonon modes in ZnSe spherical quantum dots.

2 Theoretical background

We perform a numerical calculation of dipole-active phonon modes in spherical QDs made of a polar material based on the approach proposed in [6,7]. Analytical expressions for the wave vector of the longitudinal (LO) and transverse (TO) phonon components were obtained by Roca, Trallero-Giner and Cardona [1] by imposing the condition that the phonon amplitude vanishes at the QD/medium

interface. From these calculations one can predict infrared spectra of ZnSe QDs with different radius.

In the macroscopic approach, when studying crystal lattice vibrations, one deals with the mechanical displacements $\vec{u}(\vec{x}, t)$ of ions. In the range of large wavelengths, $\vec{u}(\vec{x}, t)$ is the relative displacement of two atoms constituting a unit cell. Relative displacements of atoms of various species leads to a change in the lattice polarizability with the polarization vector $\vec{P}(\vec{x}, t)$, which can be expressed as

$$\vec{P}(\vec{x}, t) = N(\vec{x})e^*(\vec{x})\vec{u}(\vec{x}, t). \quad (1)$$

Here, $e^*(\vec{x})$ is the effective charge and $N(\vec{x})$ is the number of unit cells occupying position $\vec{x}$ in the unit. The polarization of the material can be expressed in terms of electric field strength $\vec{E}(\vec{x}, t)$. The quantities $\vec{u}(\vec{x}, t)$, $\vec{P}(\vec{x}, t)$, and $\vec{E}(\vec{x}, t)$ are connected through the system of Maxwell equations. The equation of motion may be written in the following form [6, 7]:

$$\left\{ \omega_T^2(\vec{x}) - c_T^2(\vec{x})\nabla \times \nabla + c_L^2(\vec{x})\nabla \nabla \cdot - \omega^2 \right\} \vec{u}(\vec{x}) - \left[e^*(\vec{x}) / m^*(\vec{x}) \right] E(\vec{x}) = 0, \quad (2)$$

where $\omega_T(\vec{x})$ is the frequency of a transverse optical (TO) phonon; m^* is the reduced mass of the atoms constituting the unit cell; and $c_T(\vec{x})$ and $c_L(\vec{x})$ are the transverse and longitudinal velocities of the propagation of lattice vibrations, respectively, which are proportional to the bulk LO and TO phonon dispersion curves. The next equation, which relates the electric field strength to the mechanical displacement, reads as

$$- \left[e^*(\vec{x}) / m^*(\vec{x}) \right] \nabla \cdot \vec{E} = \omega_p^2(\vec{x}) \nabla \cdot \vec{u}. \quad (3)$$

Here

$$\omega_p^2(\vec{x}) = \{4\pi e^2(\vec{x})N(\vec{x})\} / \{\epsilon_\infty(\vec{x})m^*(\vec{x})\}. \quad (4)$$

The equation for the frequencies of the spheroidal modes of angular momentum l is

$$\begin{aligned} & [2z \cos z + (z^2 - 2) \sin z] \left\{ \left[-\frac{\gamma}{x^2} \left(\frac{3}{x^2} - 1 \right) + \left(1 + \frac{2}{\epsilon_\infty} \right) \left(1 - \frac{1}{x^2} \right) \right] \sin x + \left[-\frac{3\gamma}{x^3} + \frac{1}{x} \left(1 + \frac{2}{\epsilon_\infty} \right) \right] \cos x \right\} \\ & = [\sin z - z \cos z] \left\{ \frac{1}{x} \left[-1 - \frac{2}{\epsilon_\infty} + \frac{3\gamma}{x^2 \epsilon_\infty} \right] \cos x + \frac{1}{x^2} \left[\frac{\gamma}{\epsilon_\infty} \left(1 - \frac{3}{x^2} \right) + \left(1 + \frac{1}{\epsilon_\infty} \right) \right] \sin x \right\}, \end{aligned} \quad (5)$$

$$\text{where } \gamma = \frac{\omega_{LO}^2 - \omega_{TO}^2}{\beta_T^2} R^2, \quad \omega_l^2 = \omega_{LO}^2 - \beta_L^2 \left(\frac{z}{R} \right)^2, \quad \omega_2^2 = \omega_{TO}^2 + \beta_T^2 \left(\frac{x}{R} \right)^2.$$

Here, R_0 is the QD radius. Phonons with $l_p=1$ should be infrared active, contain low-order transverse components and should thus absorb strongly in the far-infrared region [2].

3 Results and discussion

We studied experimentally a series of ZnSe QDs embedded in free-standing layers of porous Si. The size of the QDs ranges from 2.1 to 7.7 nm and was determined from the photoluminescence.

The frequencies of the coupled phonon modes with angular momentum $l_p=1$ are shown in Fig. 1. The case for $l_p=1$ modes is interesting because they represent a more general solution with both LO and TO components including a surface mode contribution. The TO components converge to the value of 207 cm^{-1} , and the LO components does to 246 cm^{-1} in the large radii limit. The band of closely spaced solutions between 207 and 246 cm^{-1} (Fig. 1) is due to modes with confinement of both the LO and TO components.

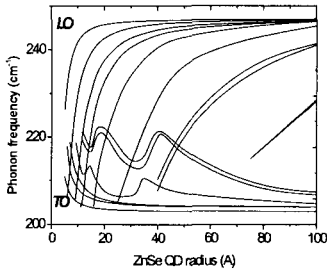


Figure 1. Frequencies of the coupled modes with $l_p=1$ for varying radius.

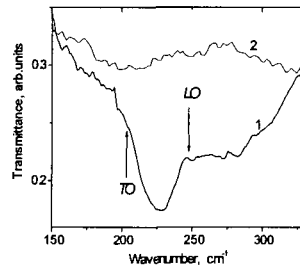


Figure 2. Room-temperature FTIR transmittance spectra of 3.2 nm ZnSe NCs embedded in *por*-Si layer (1) and pure *por*-Si layer (2).

FTIR spectra were measured with a IFS-113v Bruker Fourier-transform IR spectrometer at 300 K. In Fig. 2 experimental FTIR transmittance spectrum of 3.2 nm ZnSe QDs embedded into *por*-Si is shown (curve 1). A broad peak between the bulk TO and LO phonon frequencies, centered at $(226\text{--}231)\text{ cm}^{-1}$ dominates in the spectrum. We assign the peak in the FTIR spectrum to the coupled LO-TO modes with $l_p=1$ on the basis of our theoretical calculations (3)-(5) of the frequencies of coupled modes which Fig. 1 illustrates.

The IR spectra of pure *por*-Si layers were recorded to ensure that the observed features were not due to the host material (Fig. 2, curve 2).

We also recorded the Raman spectra in a backscattering configuration with the 488 nm line of an Ar-ion laser at low power to avoid darkening of the dots. The spectrum of 3.2 nm ZnSe QDs is shown in Fig. 3. The LO-phonon peak in ZnSe QDs is shifted to lower frequency (4.9 cm^{-1}) relative to the frequency of bulk ZnSe (indicated as LO).

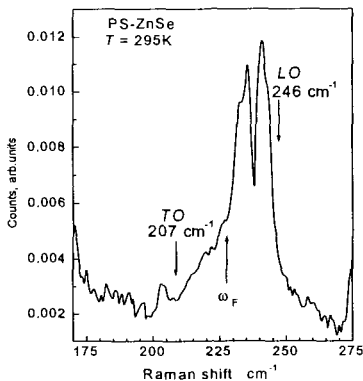


Figure 3. Raman scattering spectrum of 3.2 nm ZnSe QDs embedded in the free layer of p or-Si. Excitation wavelength: 488 nm, $T = 295\text{K}$.

Two-peak behavior of the IR spectrum shown in Fig. 2 may be due to the electrostatic Frohlich mode (ω_F) corresponding to a uniform polarization of the ZnSe sphere. The peak near ω_F (the theoretically predicted frequency is $\sim 229\text{ cm}^{-1}$) is formed by the modes whose frequencies are slightly higher than ω_F [8].

The obtained results show that the lattice dynamics of very small ZnSe NCs is similar to that of bulk ZnSe crystal in the case that dispersion curves of the main optical phonon frequencies are still correct. It is confirmed by the data obtained in [5] for CdTe QDs.

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INTRADOT CARRIER RELAXATION IN RADIATION-DAMAGED InGaAs/GaAs QUANTUM DOT HETEROSTRUCTURES

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The influence of high-energy (2.4 MeV) proton irradiation on the photoluminescence (PL), PL excitation and time-resolved PL spectra of InGaAs/GaAs quantum dots (QDs) is reported. The effect of irradiation on the PLE spectra is mainly attributed to a Fermi level shift towards the center of the gap. TRPL measurements show an evidence of carrier tunneling out of the excited QD states to adjacent defects. The ground level remains unaffected by the defects, at least up to a certain dose. Our considerations show that the dots very probably expulse radiation defects.

1 Introduction and experimental

Recently, an enhanced hardness of the quantum dot QD structures and laser diodes against particle irradiation as compared to bulk and 2D counterparts has been found [1-3]. The strong localization of the carriers inside the QDs, preventing the carriers from reaching irradiation-induced non-radiative recombination centers, has been made responsible for it. Nevertheless, an interaction of the QDs with radiation defects which leads to a reduction of resonantly excited QD PL intensity has been concluded [2]. Almost nothing is known about the microscopic details of the impact of defects on carrier recombination and intradot relaxation in QD structures. We report investigations of the photoluminescence (PL), PL excitation (PLE) and time-resolved PL (TRPL) in proton-irradiated InGaAs/GaAs QD heterostructures.

The samples (labeled A and B) were grown by MOCVD and are composed of a GaAs buffer layer on top of a GaAs substrate, an active layer with GaAs cladding layers placed between two AlGaAs barriers, and a GaAs cap on top of the structure. Sample A has an active layer composed by a QD layer (dot density $\approx (3 - 5) \times 10^{10} \text{ cm}^{-2}$) overgrown by a 2 nm $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}$ quantum well (QW). Sample B has dot density of $\sim 10^9 \text{ cm}^{-2}$ in an active layer composed by a single QD

layer. The irradiation by 2.4 MeV protons with fluences in the range from 1×10^{12} to $1 \times 10^{14} \text{ cm}^{-2}$ was carried out at room temperature.

In the TRPL measurements performed at 2K the excitation was made by a Ti:sapphire laser system, with spectrally narrow ($< 1 \text{ meV}$) 2 ps pulses. The emitted light was dispersed by a subtractive double-grating monochromator and detected with a multi-channel plate photomultiplier in the photon-counting mode with a time resolution of 20 ps.

The cw PL and PLE experiments were performed at 7 – 300K. A tungsten lamp dispersed by a 0.27 m double-grating monochromator was used as a tunable light source. The emission was analyzed by a 0.3 m double-grating monochromator and detected with a cooled Ge diode using lock-in techniques.

2 Results and discussion

Irradiation creates in semiconductors defects with deep levels that act as non-radiative recombination centers. However, an existence of stable point defects created by atomic displacements at RT inside the In(Ga)As QDs or ultra-thin QWs has never been proven. As primary defects (vacancies and interstitial atoms) are mobile at RT in GaAs [4-6] and, certainly, in InAs, it is very likely that they are captured at the interfaces (cf. [7]). The defects raise the free energy of the crystal, so

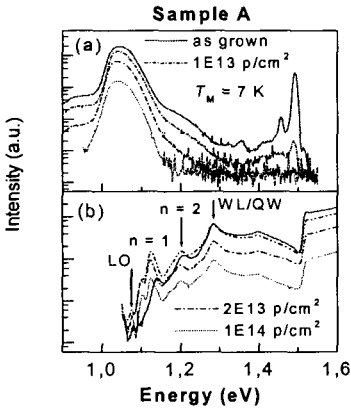


Figure 1. (a) PL and (b) PLE spectra of sample A for various proton irradiation doses, measured at 7 K. PLE spectra were recorded at the QD PL maximum.

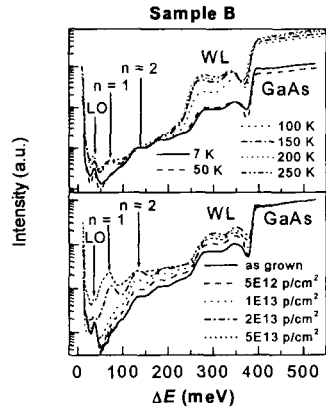


Figure 2. (a) PLE spectra vs. the excess excitation energy $\Delta E = E_{\text{exc}} - E_{\text{det}}$ of the as-grown sample B taken at different temperatures. Detection was performed at the QD PL maximum. The spectra are normalized to E_{det} and to the second excited state intensity. (b) PLE spectra of sample B for various proton doses, recorded at the QD PL maximum at 7K. The spectra are normalized to the PL intensity above the GaAs bandgap.

the QDs should expulse mobile defects into the matrix. On the other hand, it has been shown that some leakage of the wavefunction into the barrier leads to carrier escape to adjacent defects, thus deteriorating the QW and QD PL [8, 9].

Usually the defects reduce the lifetime of non-equilibrium carriers and, consequently, their diffusion length in semiconductors. However, because of the presence of the closely spaced AlGaAs barriers, the carrier capture by the QDs in our samples is not diffusion-limited. That is why a difference in the quenching factor of the PL intensity at a given irradiation dose for the above- and below-bandgap excitation for all energies above the $n = 2$ QD excited state (Fig. 1b) is not observed. Thus, the loss of carriers occurs mainly in the dots due to tunneling of carriers from the dots to adjacent non-radiative recombination centers.

Another striking feature of the PLE spectra is the *increase* upon irradiation of the PLE intensity at energies corresponding to the low-lying QD excited states (Figs. 1b, 2b). This effect is similar to that of a temperature increase (Ref. [10] and Fig. 2a) or of applying a reverse bias to a diode structure with the dots located in the space charge region [11, 12]. The common action in all the cases is the Fermi level shift towards the midgap, thus emptying the low-lying QD states from spectator carriers and allowing resonant absorption. In the case of a temperature increase, another important effect is the growth of the phonon density, which accelerates the relaxation and helps overcome the phonon bottleneck [10].

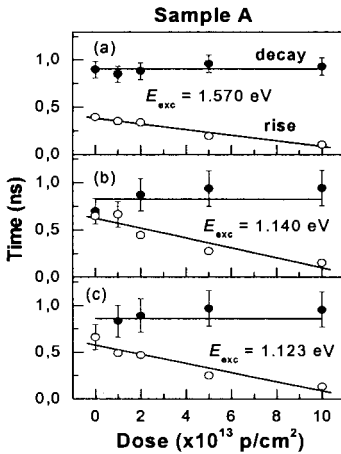


Figure 3. Rise (open circles) and decay (solid circles) time from TRPL measurements of sample A. The detection energy was at the ground state transition. (a) $E_{\text{exc}} = 1.570$ eV (above the GaAs bandgap); (b) $E_{\text{exc}} = 1.140$ eV (a sublevel of the 1st excited state); (c) $E_{\text{exc}} = 1.123$ eV (another sublevel of the 1st excited state).

The results of the TRPL measurements performed on sample A as a function of the irradiation dose, for resonant and non-resonant excitation, corroborate the PLE data. No influence of the irradiation on the PL decay kinetics from the ground state is observed (Fig. 3). However, the rise time shortens by about a factor of 4 for the maximum dose used. This means that the rise time shortening upon above-bandgap excitation is caused by a carrier loss in the QDs and not by any reduction of the diffusion length in the barrier or the WL. The effect can be explained by tunnel escape of the carriers to adjacent defects. The ground state, having a more localized wavefunction than the excited ones, remains essentially “undamaged”. Contrary to earlier measurements on electron irradiated QDs [13], no development of a second, shorter, decay time has been observed. We attribute this difference to the heavier damage caused by the electron irradiation used in Ref. [13].

3 Conclusion

Surprisingly, an increase of the ground state PL yield upon resonant excitation into the low-lying QD states of InGaAs/GaAs QD heterostructures has been observed upon proton irradiation. The reason is lowering of the Fermi level and recharging of the dots due to electrical compensation of the barrier material by radiation defects, which allows the intradot light absorption to occur. The PL rise time gets shorter with increasing irradiation dose owing to a carrier escape out of the excited QD states to adjacent defects. For the doses used, the decay time of the ground state PL remains unaffected, proving a high radiation hardness of the dots. Along with the high localization of the wavefunction in the dots, a probable expulsion of the mobile defects out of the dots may be responsible for this hardness.

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ENHANCED PHOTOLUMINESCENCE OF Tb^{3+} AND Eu^{3+} INDUCED BY ENERGY TRANSFER FROM SnO_2 AND Si NANOCRYSTALLITES

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Terbium (Tb^{3+}) and europium (Eu^{3+}) - doped tin oxide (SnO_2) was prepared using sol-gel method to form $\text{SnO}_2:\text{Tb}^{3+}/\text{Si}$ and $\text{SnO}_2:\text{Eu}^{3+}/\text{Si}$ nanocomposites. The Rutherford Back Scattering (RBS) measurements show an uniform repartition of rare earth ions in the SnO_2 layer. The High Resolution Transmission Electron Microscopy (HRTEM) observations revealed the presence of small crystallites of SnO_2 where the average size ranges from 3 to 10 nm. The mechanism of rare earth excitation and emission is discussed. $\text{SnO}_2:\text{Tb}^{3+} + \text{Eu}^{3+}/\text{Si}$ nanocomposites are formed using the same method by doping the gel with Tb^{3+} and Eu^{3+} . The mechanism of emission is discussed and we show that the transfer of excitation occurs between rare earth ions.

1 Introduction

Recently, a great interest is devoted to transition metal and rare earth ion – doped nanoparticles because of their practical application. In particular, Bhargava et al. showed strong orange luminescence from Mn^{2+} ions doped ZnS nanoparticles [1]. They attribute the PL enhancement to the quantum confinement affecting photogenerated carriers and energy transfer to rare earth ions. Since their work, there are many reports on optical properties of the ion-doped nanoparticles [2-6]. Sol-gel glasses reveal interesting fluorescence of transition metal ions and rare earth ions. However, the mechanism of fluorescence remains not well studied.

In this paper, we present the results of PL measurements of SnO_2 :rare earth ions deposited on Si substrates. The repartition of rare earth ions in the SnO_2 layer is shown from RBS and EDX analysis. The excitation process is discussed.

2 Experimental

SnO_2 doped with Tb^{3+} was prepared by the sol-gel technique [7]. In the synthesis of undoped and Tb^{3+} doped SnO_2 sol-phases $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and TbCl_3 were used as precursors and absolute ethanol as a solvent. The concentration of Tb^{3+} is estimated to be 3% in relation with the Sn content in the sol.

Si (100) p-type substrates with one polished face served as substrates for SnO_2 . They were rinsed in HF solution to remove all oxide on the surface. Then the substrate was dipped in the sol (SnO_2 : Tb^{3+}), dried at 80°C and annealed for 20 min at 700°C . Multi-impregnation is performed to assure a uniform distribution of SnO_2 on the substrate. The SnO_2 : Eu^{3+} /Si nanocomposites are formed by using the same method.

PL measurements were performed using a triple monochromator and an argon laser as an excitation source. The repartition of terbium, tin and oxygen in the SnO_2 layer is controlled by RBS of 2 MeV He^+ particles.

3 Results and discussion

RBS measurements show that the layer on the Si substrate is formed by Sn, O and Tb (Fig. 1). The large band related to Tb^{3+} is an indication of the uniform distribution of these ions over the SnO_2 layer.

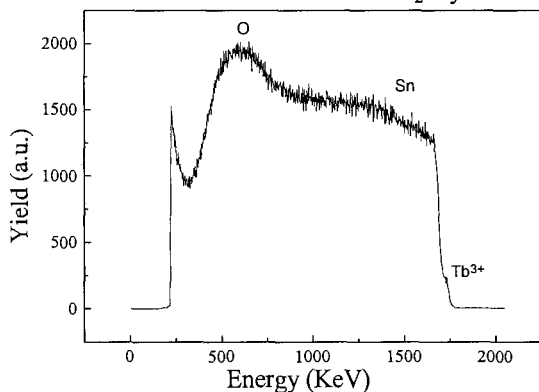


Figure 1. RBS spectrum of SnO_2 : Tb^{3+} /Si after annealing at $T=700^\circ\text{C}$.

Fig. 2 shows a HRTEM image taken from SnO_2 : Tb^{3+} deposited on the Si substrate. More crystallites are polycrystallite, with the lattice fringes in the grains corresponding to main reflections of the tin oxide (SnO_2) structure. The grains of cassiterite have a spherical morphology with a diameter ranging from 3 to 10 nm. The EDX spectrum recorded along the cross section of the sample proves the presence of Tb^{3+} ions inside SnO_2 crystallites. The diagram shows the presence of two peaks associated with Tb^{3+} ions and other peaks with higher intensity associated with O ($\approx 66.3\%$) and Sn ($\approx 32.5\%$) atoms. The Tb^{3+} content in SnO_2 matrix is about 1.5%.

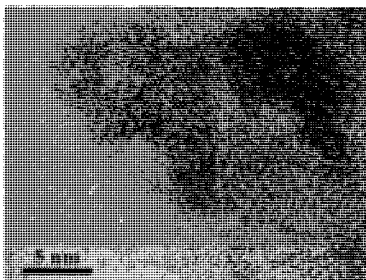


Figure 2. HRTEM image of $\text{SnO}_2:\text{Tb}^{3+}$.

Fig. 3 shows PL spectra for $\lambda_{\text{exc}}=488 \text{ nm}$ of $\text{SnO}_2:\text{Tb}^{3+}/\text{Si}$ (a) and of $\text{SnO}_2:\text{Tb}^{3+}/\text{porous silicon}$ (b) after annealing at 700°C for 20 min. The inset shows the PL spectra as a function of Tb concentration in the SnO_2 sol. The peaks intensities increase with the increase of Tb concentration. The PL spectra show four peaks corresponding to the characteristics $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($j=3-6$) transitions in Tb^{3+} ions. The peaks relatives to the $^5\text{D}_4 \rightarrow ^7\text{F}_{0,1,2}$ appear only for high luminescence of terbium like for $\text{SnO}_2:\text{Tb}^{3+}/\text{PS}$ (spectrum (b)) and for $\text{SnO}_2:\text{Tb}^{3+}/\text{Si}$ with the high concentration of terbium. The annealing temperature corresponding to the crystallization of SnO_2 is below 450°C [7]. At such temperatures polycondensation and densification may have occurred and cassiterite material must have been formed. The SnO_2 crystallites absorb at the energy corresponding to 488 nm (inset of Fig. 1). They can transfer the excitation to rare earth ions. Furthermore, the crystallite size is in the range of $3\text{-}10 \text{ nm}$, which serves to create a quantum confinement effect of carriers and contribute to the enhancement of Tb fluorescence. The PL peaks of $\text{SnO}_2:\text{Tb}^{3+}$ on PS are resolved. They are 10 times higher than those form a Si substrate. The observed increase of PL intensity can be assigned to energy transfer to Tb^{3+} ions from Si nanocrystallites where the absorption is important at 488 nm .

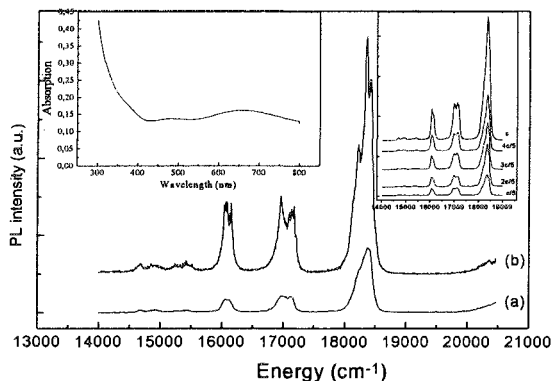


Figure 3. PL spectra of $\text{SnO}_2:\text{Tb}^{3+}/\text{Si}$ (a) and $\text{SnO}_2:\text{Tb}^{3+}/\text{PS}$ (b) after annealing at 700°C . Inset 1: Absorption spectrum of $\text{SnO}_2:\text{Tb}^{3+}$. Inset 2: PL dependence on Tb^{3+} concentration in SnO_2 .

The Tb^{3+} ions in SnO_2 nanocrystallites are excited by two ways. One is direct excitation of Tb^{3+} ions since their PL depends strongly on the excitation energy (the PL peaks of terbium appear essentially after excitation at 488 nm) [8]. The other is from excitation into the conduction band of the host crystal followed by an

excitation transfer to Tb^{3+} ions to cause the emission. In [9], it was shown that fluorescence of rare earth depends strongly on SnO_2 concentration in SiO_2 glasses. The fluorescence intensity increases with SnO_2 concentration due to energy transfer from SnO_2 nanocrystallites to rare earth ions. They show that the increase of optical absorption with SnO_2 content leads to an increase of the energy transferred to rare earth ions.

Fig. 4 shows PL spectra for $\lambda_{exc}=465.8$ nm of $SnO_2:Eu^{3+}/Si$ nanocomposites after annealing at different temperatures. The optimized PL spectrum is found after annealing at $900^\circ C$. The peaks become resolved and the PL intensity increases considerably showing an activation of Eu^{3+} ions in SnO_2 . We present also in Fig. 3 the optimized PL spectrum of $SnO_2:Eu^{3+}$ in a PS matrix. It is clear that the performance of europium emission is highly improved in PS.

The enhancement can be explained also by an excitation transfer from Si nanocrystallites to Eu^{3+} ions. Other authors [10] have shown similar results by comparing the PL of Eu^{3+} in silica gel and in silica gel with colloidal cadmium sulfide. They show that CdS nanoparticles enhanced Eu^{3+} fluorescence due to energy transfer from a surface trap in the CdS particles to Eu^{3+} ions.

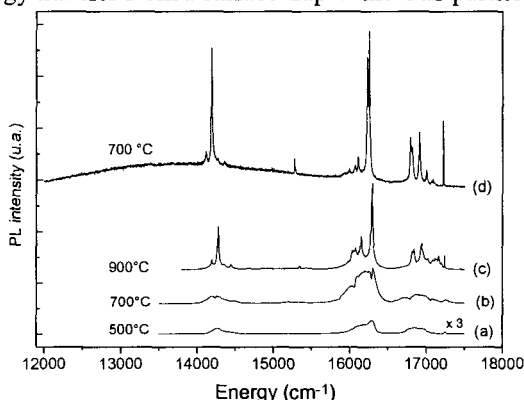


Figure 4. PL dependence of $SnO_2:Eu^{3+}/Si$ on annealing temperature (a,b,c) and PL spectrum of $SnO_2:Eu^{3+}/PS$ after annealing at $700^\circ C$.

$EuCl_3$ crystals are added to the $SnO_2:Tb^{3+}$ sol. $SnO_2:Tb^{3+}+Eu^{3+}/Si$ nanocomposites were formed by the same procedure. The corresponding PL spectrum for $\lambda_{exc}=488$ nm shows (Fig. 5) intense peaks related to intra shell transitions in Tb^{3+} and Eu^{3+} ions. These peaks are more intense and better resolved than those from $SnO_2:Tb^{3+}/Si$. The corresponding PL spectrum for $\lambda_{exc}=465.8$ nm shows only the peaks related to Eu^{3+} ions but their intensities are 20 times lower than at $\lambda_{exc}=488$ nm. We noted that Tb^{3+} ions do not emit under $\lambda_{exc}=465.8$ nm and Eu^{3+} ions present the strong PL for the latter case. As the emission of Eu^{3+} in $SnO_2:Tb^{3+}+Eu^{3+}/Si$ is 20 times higher for 488 nm than for 465.8 nm, we think that a process of radiative excitation transfer occurs from Tb^{3+} ions to Eu^{3+} ions. Therefore, the Eu^{3+} ions in the matrix seem to be excited by three ways: direct excitation, excitation transfer from SnO_2 nanocrystallites and radiative excitation transfer from Tb^{3+} ions. The PL of Tb^{3+} ions is also highly enhanced by codoping of

SnO₂ with Eu³⁺ ions. Each process seems to be due to an excitation transfer in the reverse order from Eu³⁺ to Tb³⁺ or to an increase of excitation transfer from SnO₂ or to an increase of the quantum confinement effect since SnO₂ crystallites size decreases with doping [7].

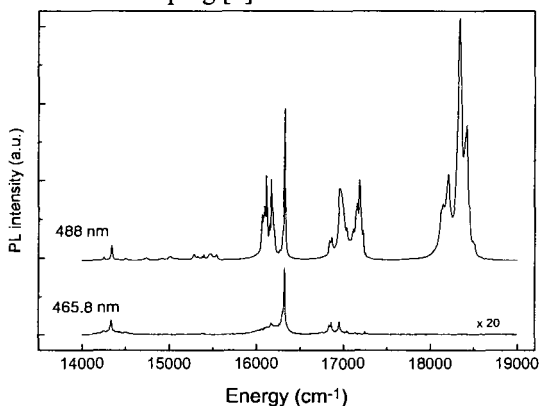


Figure 5. PL spectra of SnO₂:Tb³⁺+Eu³⁺/Si for the corresponding excitation rays.

4 Conclusion

We have elaborated highly luminescent nanocomposites based on SnO₂ and rare earth ions using the sol-gel method. RBS and HRTEM analysis show a uniform repartition of rare earth ions in SnO₂ films and the formation of crystallites after subsequent annealing. The PL can be attributed to direct excitation of rare earth ions and to an excitation transfer from SnO₂ crystallites. The emission is highly enhanced by doping SnO₂ sol with Tb³⁺ and Eu³⁺ ions. These preliminary positive results open the way towards solid state electrodes for electroluminescence applications of rare earth doped transparent oxides like SnO₂ as a transparent n-type degenerated semiconductor electrode deposited on Si substrates.

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WHISPERING GALLERY MODE EMISSION FROM A CORE-SHELL SYSTEM OF CdTe NANOCRYSTALS ON A SPHERICAL MICROCAVITY

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We have studied the optical properties of a novel microcavity - quantum dot system consisting of a melamine formaldehyde latex microsphere coated by a thin shell of CdTe nanocrystals. The coupling between the emission from nanocrystals and spherical cavity modes was realized. Periodic narrow peaks of the emission spectra corresponding to the whispering gallery modes were detected and a threshold behavior of the emission intensity on excitation power was observed.

1 Introduction

Whispering gallery mode (WGM) oscillations within a single spherical microcavity doped by semiconductor nanocrystals have been a subject of intense theoretical and experimental study for last two years [1-5]. The combination of the high quality factor (Q) and the small mode volume of glass microspheres with tunable emission properties of CdSe nanocrystals (NCs) has made it possible to get extremely narrow resonant structure in emission spectra [1], to observe the modification of photoluminescence (PL) decay lifetimes [4,5] and lasing [2,5]. However, whispering gallery modes are only demonstrated for glass microspheres doped by CdSe NCs. Recently, we have developed the core-shell system consisting of a melamine formaldehyde (MF) latex microsphere coated by CdTe NCs. The high optical transparency, thermal and mechanical stability of MF make it interesting as a candidate in optical applications. On the other hand, the lowest cutoff wavelength of telecommunication fibers is just in the spectral region of CdTe NCs emission.

2 Experimental details

CdTe NCs capped with thioglycolic acid were synthesized in aqueous medium as described elsewhere [6]. Two colloidal solutions of nanocrystals with PL maximum at 595 (4.4 nm diameter) and 635 nm (5.1 nm diameter) and PL quantum efficiency of $\sim 25\%$ at room temperature were used for coating of MF microspheres (5.2 μm in diameter) utilizing the layer-by-layer deposition technique [7].

Absorption and PL spectra of colloidal NCs were measured using a Shimadzu-3101 and Spex Fluorolog spectrometers, respectively. The PL spectra from a single microsphere were recorded using a RENISHAW micro-Raman system (1800 mm^{-1} grating, $> 1\text{cm}^{-1}$ resolution, $\times 100$ objective). An Ar^+ laser (wavelength 514.5 nm, 25 mW power) was used in the micro-PL measurements.

3 Results and discussion

The optical spectra of colloidal CdTe NCs in water are presented in Fig. 1, demonstrating the pronounced peak in absorption and single featureless PL band. The blue shift of the NCs absorption band by $\sim 570\text{ meV}$ with respect to bulk CdTe indicates the strong electronic quantum confinement effect.

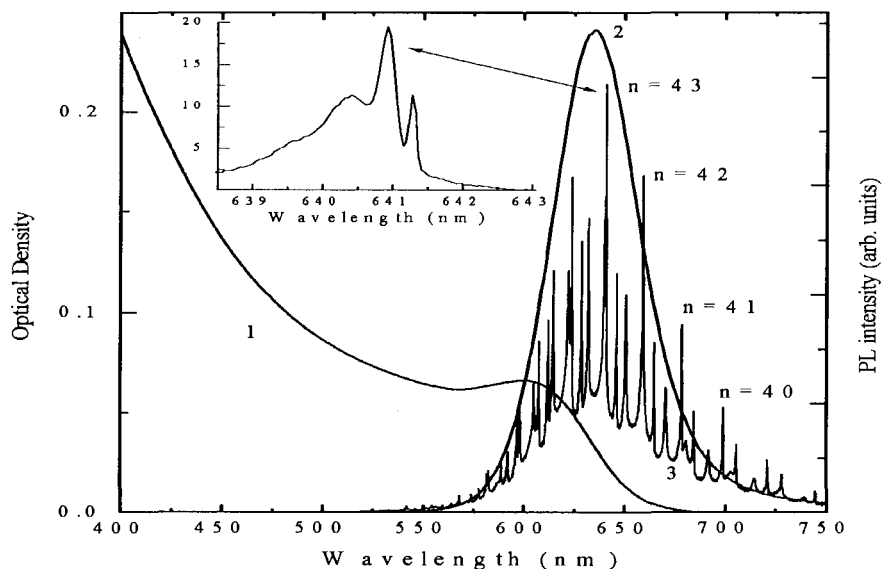


Figure 1. Room temperature absorption (1) and PL spectra of CdTe NCs in aqueous solution (2) and PL spectrum from a single MF microsphere coated by a monolayer shell of CdTe NCs (3). Inset shows fine structure of the PL peak with $n = 43$.

The emission spectra of a single MF/CdTe NCs sphere exhibit a sharp periodic structure. The placement of the WGM resonances can be characterized by mode number n , which is equal to the circumference divided by the wavelength of the light propagating within the microsphere. As one can see from Fig. 1, the WGM peaks with different n are superimposed on a background signal arising from part of NCs emission. High resolution of the detection system allows us to detect the fine structure of each WGM peak (inset in Fig. 1). At the wavelength of $n=43$ peak, the Lorentzian fit gives the linewidth of the cavity mode: $\gamma = 0.0011$ eV, which allows to estimate Q factor: $Q_{43} = \hbar\omega_{43}/\gamma \sim 1700$. At $\lambda_{41} = 678.3$ nm ($\hbar\omega_{43} = 1.83$ eV) the linewidth for the resonance mode is about $\gamma = 2\hbar\Delta\omega = 0.0007$ eV. The Q value is then ~ 2600 , being much higher than on the low-wavelength side. It is well known that absorption or gain alter the Q value. In our case the absorption coefficient is reduced at the high-wavelength part of the PL band, allowing a higher Q factor.

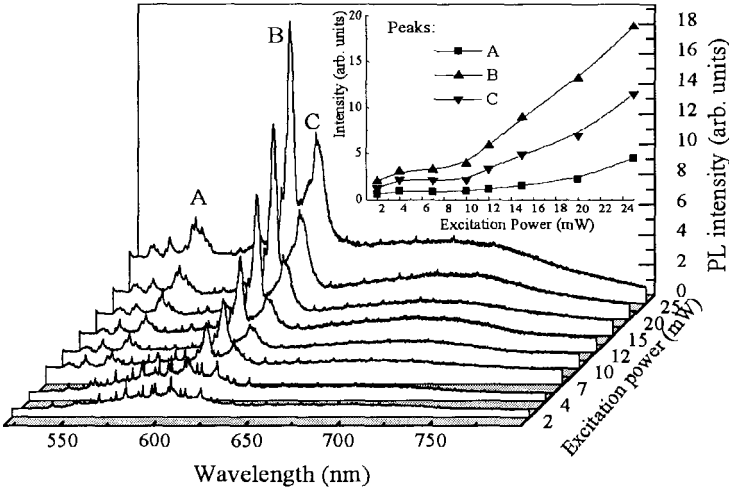


Figure 2. PL spectra of a single MF/CdTe NCs sphere at different pump energies. The inset shows the emitted intensity at 555 nm (peak A), 607 nm (peak B) and 621 nm (peak C).

Because of high Q factor of MF microspheres and the very narrow WGM peaks, spherical microcavities are very promising systems for the design of an optically pumped microlaser emitting at room temperature [5]. In order to investigate possibility of laser operation in this spectral region, we studied PL spectra of a single MF microsphere coated by a shell of CdTe NCs (4.4 nm diameter) under optical excitation of various intensity (Fig. 2). A sharp peak with a Lorentzian lineshape and a full width at half-maximum of 2.3 nm emerges at the 607 nm and grows to dominate the entire emission spectrum with increased excitation power. The intensity of this peak increases faster than intensity of the background luminescence. A clear threshold at ~ 10 mW can be seen in dependence of emission intensity on pump power. This feature can be quoted as evidence of

lasing. Also additional PL peaks (A and C) appear in the spectra as the pump energy increases. Both of them do not show a clear threshold behavior in the $I_{PL} = f(I_{pump})$ dependence.

In conclusion, we have demonstrated the resonance modes in a system consisting of a spherical microcavity coated by a thin CdTe NCs shell. Our results show that lasing in MF/CdTe NCs system is possible even if the quality factor of the microcavity is not very high. Microspheres coated by CdTe nanocrystals may therefore be useful for a variety of photonic applications.

Acknowledgements

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PHOTOLUMINESCENCE UP-CONVERSION IN CdTe NANOCRYSTALS

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We report on the efficient photoluminescence up-conversion in colloiddally synthesized CdTe nanocrystals. We demonstrate that the efficiency of photon energy up-conversion and the magnitude of the spectral shift can be controlled by: (i) the size of the nanocrystals; (ii) the temperature dependence of the excited state absorption coefficient; (iii) the excitation intensity. We suggest that intrinsic gap states are involved as intermediate states in the up-conversion rather than nonlinear two-photon absorption or Auger processes.

1 Introduction

Anti-Stokes photoluminescence (ASPL) or photon energy up-conversion (UC), in semiconductor quantum dots has attracted much attention recently [1-5]. In general, the energy up-conversion is usually achieved by Auger process [5], a nonlinear mechanism such as two-photon absorption [5] or by thermal activation. [4,6]. In this work we report on the ASPL at room temperature and very low excitation intensity in colloidal CdTe nanocrystals (NCs).

2 Experimental Details

CdTe NCs of different sizes were synthesized in aqueous solution by reaction of cadmium perchlorate with H_2Te gas following the method of Ref. [7].

Absorption spectra were measured using a Shimadzu UV-3101 PC spectrometer. The PL spectra were recorded using a Spex Fluorolog spectrometer by exciting the samples with a Xenon lamp. A Xenon lamp or He-Ne laser ($\lambda = 632.8$ nm, output power of 2 mW) was used for ASPL measurements. A cut-off filters or an interference 633 nm filter was used to eliminate spurious laser lines from appearing in the ASPL spectra.

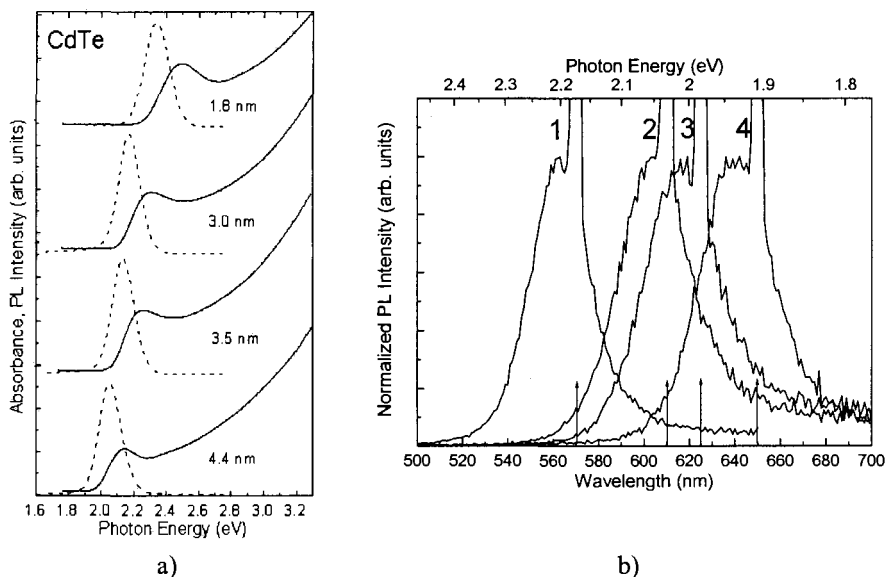


Figure 1. (a) Room-temperature absorption and SSPL of CdTe NCs with different sizes. (b) ASPL spectra of CdTe NCs with different sizes (1 – 1.8 nm; 2 – 3.0 nm; 3 – 3.5 nm; 4 – 4.4 nm). Wavelengths of the excitation are indicated by arrows.

3 Results and discussion

Fig. 1a demonstrates the evolution of optical properties of CdTe NCs as their size increased from 1.8 to 4.4 nm. The well-pronounced absorption peaks are indicative of a narrow size distribution of CdTe NCs, which was estimated to be about 10-12%. The steady-state PL (SSPL) spectrum excited by the Xe-lamp ($\lambda_{\text{ex}} = 400$ nm) consists of one sharp peak of band-edge emission.

The PL spectra excited with the energies less than peak position of SSPL (i.e. $<E_g$) show well resolved ASPL bands (Fig. 1b) in the high-energy part of the spectra of all samples. The maximum efficiency for energy up-conversion in the sample of 3.5 nm CdTe NCs was estimated to be about 3.34×10^{-4} % relative to the absorbed Xenon lamp power at 625 nm ($h\nu = 1.98$ eV) at room temperature.

The maximum up-converted blue shift (ΔE) can be defined as a difference between the excitation energy and the energy value at which an exponential fit of the ASPL spectrum crosses the average background noise level [3]. Using this procedure maximum value of $\Delta E = 350$ meV was obtained for excitation of CdTe NCs of 3.5 nm.

It was found that ASPL intensity depends linearly on excitation intensity for all samples. This feature clearly indicated that two-photon absorption (quadratic

dependence on excitation intensity) or Auger recombination (cubic dependence on excitation intensity) could not be the cause of the observed photon energy up-conversion.

At high temperatures ASPL can be observed as a result of energy accumulation of the excited electron-hole pair from the phonon bath [4,6]. In that case the intensity of ASPL should grow with rising temperature because of the increase of the phonon occupation number. It was found indeed that the ASPL intensity increases dramatically with temperature (Fig. 2). At the same time, the Stokes-shifted PL shows thermal induced quenching and broadening. The ASPL linewidth shows additional broadening with decreasing excitation energy (from 120 meV at $\hbar\omega_{\text{ex}}=2.0$ eV to 150 meV at $\hbar\omega_{\text{ex}}=1.95$ eV).

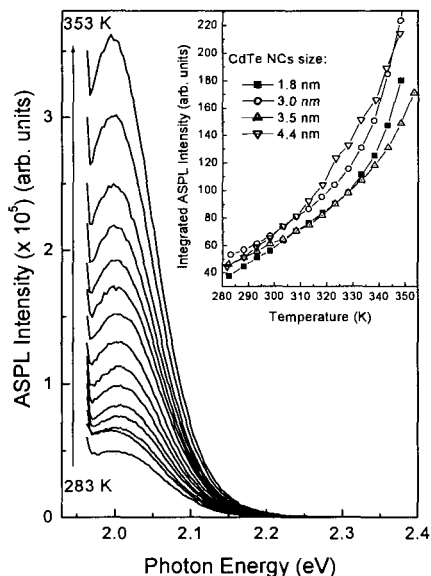


Figure 2. Temperature behavior of the ASPL band in 3.5 nm CdTe NCs. Inset: Variation of the integrated intensity of the UCPL with temperature for all samples studied.

Although these experimental findings testify to an important role of electron-phonon interactions in UC processes in CdTe NCs, this mechanism alone is not a sufficient explanation of all the experimental results. The thermal energy available from the phonon bath is too small to explain the obtained ΔE value.

Based on the above discussed experimental results and data from previous studies we propose that the observed UC PL originates from cascade a phonon-assisted excitation via a set of below-gap states. The photon energy UC mechanism responsible for production of the ASPL in CdTe QDs is therefore attributed to the excitation from the valence band into one of the below-gap trap states located near the CB (CBtrap). Thermally activated retrapping from the CBtrap state causes repopulation of the trap states and possible transitions to the conduction band

(detrapping) followed by recombination to the valence band. Based on the finding that the ASPL linewidth does not follow the size distribution of the NCs we suggest the involvement of shallow electron traps rather than “dark” exciton as CBtrap states at room temperature.

At higher temperatures thermal detrapping is more significant, and it gives a rise of the ASPL intensity. It is reasonable to propose an activation energy E_{act} for the detrapping process. From analysis of the Arrhenius plots we estimated E_{act} to be in the range of 300-360 meV. Although a simple model proposed in the present work satisfies all observed results, a complete description of the photon energy UC in CdTe NCs requires knowledge of the nature and the density of localized states as well as the corresponding electron-phonon coupling which are poorly understood so far.

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ENHANCED PHOTOLUMINESCENCE OF SEMICONDUCTOR NANOCRYSTALS NEAR METAL COLLOIDS

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We present the observation of a distance-dependent enhancement and quenching of semiconductor nanocrystal photoluminescence near gold colloids. A layer-by-layer polyelectrolyte deposition technique was used for varying the distance between gold nanoparticles and quantum dots. The maximum enhancement by a factor of five is achieved for a 9-layer spacer (11 nm).

1 Introduction

The modification of photoluminescence (PL) from atoms and molecules located near metal nanostructured surfaces and nanobodies is an interesting subject in nanoscience. Its study gives new insights into the basic aspects of field-matter interaction [1,2]. Semiconductor nanocrystals (quantum dots, QDs) possess a number of advantageous features as light emitters [3] and fluorescent labels [4] as compared to ionic and molecular chromophores.

In the present paper, we report on observation of the pronounced enhancement of photoluminescence of semiconductor nanocrystals near nanostructured metal surfaces which is shown to depend essentially on nanocrystal-metal spacing. Unlike conventional SERS, the surface enhanced PL should exhibit non-monotonous character with distance between emitting dipole (QD) and metal surface (Au colloid). The reason is that at smallest distances when QDs and colloidal particles are in close contact, the QD emission should be damped due to resonant energy transfer (RET) from photoexcited QDs to metal colloidal nanoparticles. Enhancement of photoluminescence (PL) is possibly promoted by surface plasmons excited in the metal. So, at a certain distance the enhanced QD emission would exhibit a maximum. We use a polyelectrolyte multilayers as the most appropriate

spacer of different thickness between quantum dots and supported gold colloidal film.

2 Experiment

Layer-by-layer deposition from aqueous solutions of two types of oppositely charged polymers, usually positively charged polydiallyldimethylammonium chloride (PDADMAC, polycation) and negatively charged sodium polystyrene sulfonate (PSS, polyanion) produces a multilayer film via electrostatic interaction between oppositely charged macromolecules. The thickness of such films can be controlled precisely by a number of deposited layers from approximately 1.2 nm for one layer to 33.9 nm for 21 layers [5]. Finally, oppositely charged (relatively to PDADMAC) QDs can be deposited on the surface of the polyelectrolyte spacer as a submonolayer film.

(CdSe)ZnS core-shell QDs were synthesized via the standard high temperature reaction in TOPO/HDA mixture [6]. The diameter of QDs is about 8 nm and PL band is centered at 645 nm. QDs were solubilized in water according to known procedures [7] using sodium mercaptoethylsulfonate (SMES) as solubilizing agent which brings also strong surface negative charge on QDs. Gold colloids of 12-15 nm in diameter were synthesized by citrate reduction of diluted HAuCl_4 aqueous solution [8]. Gold nanoparticles are charged negatively due to chemisorption of citrate ions. A monolayer of gold nanoparticles was formed by electrostatic deposition onto glass slides covered with a layer of polycation. The absorption spectrum of gold colloidal film shows the well-known surface plasmon (SP) band around 550 nm (Fig. 1).

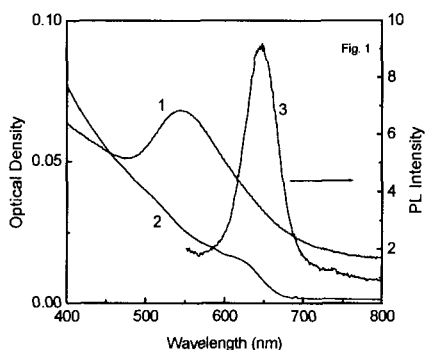


Figure 1. Absorption spectra of Au colloidal film on glass (1), (CdSe)ZnS QDs film on glass (2) and PL spectrum of QDs submonolayer on glass (3). $\lambda_{\text{PL excitation}} = 450\text{nm}$.

We examined the morphology of our gold colloidal films on glass with atomic force microscopy and found that the gold nanoparticles form close-packed monolayer with a small amount of aggregates. To cover the gold film with

polyelectrolyte layers we adopted the method described in Ref. 5. The last layer was always PDADMAC. The sample was dried at room temperature and diluted aqueous solution of QDs stabilized with SMES was dropped and gently distributed over the whole sample surface. It is important to note, that every time we dropped the same amount of QDs solution on each sample. After drying, it gave us a row of samples in the form of gold colloidal films covered by a different thickness of polyelectrolyte spacer but *equal* amount of QDs on each sample.

PL spectra from the samples with different thickness of polyelectrolyte spacer have been measured with the excitation wavelength, corresponding to the maximum of plasmon resonance in the absorption spectrum of the gold colloidal film ($\lambda = 550$ nm). The enhancement of PL is expected to be most pronounced when excited at the frequency of surface plasmon resonance in gold colloids.

3 Results and discussion

Fig. 2 shows the magnitude of the QDs PL band for different thickness of polyelectrolyte spacer up to ~ 30 nm (19 layers) [5]. If the number of layers is further increased, the PL signal drops down to the level of QDs on glass without gold colloids (the reference sample). Note, that polyelectrolyte spacer itself should not influence the PL signal from QDs.

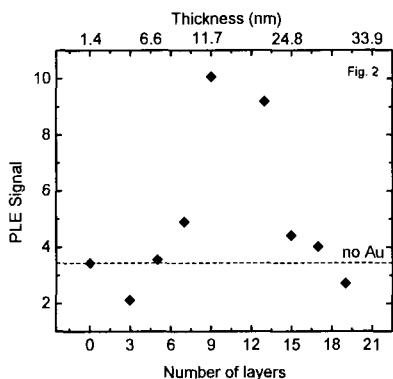


Figure 2. QD-PL intensity versus number of polyelectrolyte layers between QDs and gold colloids. The horizontal dashed line shows the PL intensity of the same amount of QDs deposited on glass without gold colloids (a reference sample). $\lambda_{\text{excitation}} = 550$ nm.

Both PDADMAC and PSS do not absorb in the visible and do not quench the QDs emission. The important result is that the PL intensity is sensitive to the distance between gold colloids and QDs and exhibits a maximum at around 9 layers (11 nm) of the polyelectrolyte film. In the absence of polyelectrolyte layers (zero point in Fig. 2 but yet non-zero distance between QDs and gold colloids since QDs carry approximately 1 nm in length the surface monolayer of SMES molecules) the PL signal is dropped by a factor of 3 relatively to the maximum. This observation is in agreement with recent reports about quenching of PL due to RET observed for

molecular systems at metallic surfaces [9,10]. Surprisingly, the 19-layer polyelectrolyte spacer gives rise to a PL signal which is comparable to that for zero layers within the experimental error. We may conclude that RET which is mainly responsible to a quenching of QD emission is very efficient at very short distances between QDs and gold colloids and can completely compensate the effect of enhanced PL.

In conclusion, we have studied the sensitivity of enhanced luminescence to the distance «quantum dot-gold colloid». We propose to use layer-by-layer approach for changing the distance between light emitters and metal surface in order to obtain the optimal conditions for enhancing or quenching fluorescence of quantum dots.

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EVOLUTION OF OPTICAL PHONONS IN CdSe/ZnS QUANTUM DOTS: RAMAN SPECTROSCOPY

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The evolution of optical phonon spectra of colloidal core/shell CdSe/ZnS nanocrystals with an increase of the shell thickness from 0.5 to 3.4 monolayers have been studied by resonant Raman spectroscopy. The results show that at a thickness of about 2ML the surface of the CdSe core is mainly defect free although the structure of the shell is not established yet. The latter occurs at the thickness more than 3.4 ML where the shell is, most likely, amorphous. It is concluded that the defect-free core/shell interface is more important for producing high-luminescence QD structures than the increase of the shell thickness.

1 Introduction

Highly-luminescent II-IV semiconductor nanocrystals, or quantum dots (QDs) have attracted much attention because of their applications in optoelectronics, non-linear optics and biology. It is known that the photoluminescence (PL) efficiency of QDs can be improved by growing a shell of a wide-band gap semiconductor around the QD core. A good example is the CdSe/ZnS core/shell QDs that possess high PL quantum yield (>50%) with a narrow PL line [1]. However, the dependence of PL efficiency on the shell parameters, e.g., structure of the shell (amorphous vs. crystal) and the quality of the core/shell interface have yet to be clarified. In this paper, we present results of optical phonon Raman studies of CdSe/ZnS QDs with different thickness of the ZnS shell which allow one to investigate the above mentioned problem.

2 Experimental

Several samples of CdSe/ZnS QDs with a CdSe core size of 4 nm and different thickness of ZnS shell measured in monolayers (ML) have been studied at RT. The QDs were prepared by an organometallic synthetic approach in a three-component hexadecylamine – trioctylphosphine oxide – trioctylphosphine mixture [1]. All samples exhibited a PL in the region of 594-600 nm with quantum yield above 50%. The size of the core (4 nm) and the width of the QD size distributions (from 8% to 12%) were estimated from absorption spectra as described in Ref. [1].

For Raman measurements the QDs were deposited on a Si wafer from the toluene solution. Their Raman spectra were excited by a 488 nm line of an Ar⁺ laser with power of 0.5-0.8 mW. The micro-Raman spectrograph (Renishaw-1000) equipped with x20 objectives and cooled CCD cameras were used in the experiments. Each spectrum was averaged over about 20 measurements with accumulation time of 20 s. The PL backgrounds due to the lowest energy optical transition of QDs were subtracted.

3 Results

The Raman spectra of the samples in the region of the CdSe LO phonons is shown in Fig. 1. The uncapped, or free-standing QDs shows slightly asymmetrical Raman

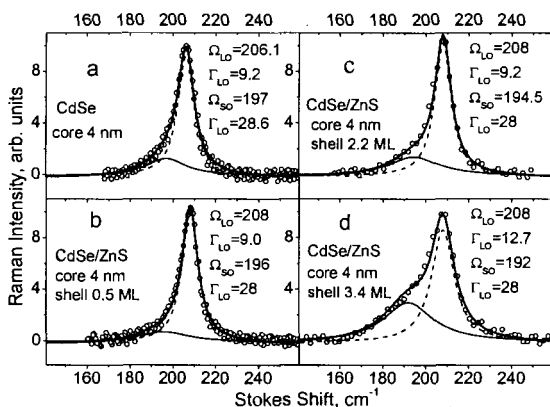


Figure 1. Raman spectra of the CdSe/ZnS QDs with different thickness of ZnS shell shown in ML. The energies of the LO and SO phonons of the CdSe core are shown together with corresponding linewidths.

signal composed of a large LO-phonon band and a weak low-energy shoulder. The structure as well as analogous ones in spectra of other samples were fitted by sum of two Lorentzians. As seen in Fig. 1a for the free-standing QDs, the energy of the

LO-phonon, Ω_{LO} of 206.1 cm^{-1} is smaller than the corresponding bulk value of 210 cm^{-1} [3] by 3.9 cm^{-1} . The shift comes from two sources: a red shift due to confinement of optical phonons [2], which is expected to be $\sim 4.7 \text{ cm}^{-1}$ for 4 nm CdSe QDs and a blue shift from the QD lattice contraction due to an increase of the surface tension force [4]. As observed, both mechanisms contribute to the shift. A 9.2 cm^{-1} width (FWHM, Γ) of the LO-phonon line in our experiment coincides with that measured by a size-selective resonant Raman spectroscopy for 4.2 nm CdSe QDs [2].

The 197 cm^{-1} shoulder, most likely, comes from the CdSe surface optical modes (SO) [5]. Their energies are determined by the energy of the TO phonons, Ω_{TO} , the shape of the QDs [6], and dielectric constants of the core and surroundings which

for spherical QDs can be presented as [5]: $\Omega_{SO} = \Omega_{TO} \left[\frac{\varepsilon_0 \times l + \varepsilon_M(l+1)}{\varepsilon_\infty \times l + \varepsilon_M(l+1)} \right]^{1/2}$, where

ε_0 and ε_∞ are the static and the high-frequency dielectric constants of the bulk CdSe, ε_M is the static dielectric constant of the surroundings, and l is the SO-phonon angular momentum. Only SO modes with $l=1$ are allowed in the Raman process [5],

and $\Omega_{SO} = \Omega_{TO} \left[\frac{\varepsilon_0 + 2\varepsilon_M}{\varepsilon_\infty + 2\varepsilon_M} \right]^{1/2}$. If we suppose $\varepsilon_M=1$ (air) for the free-standing QDs

and take $\Omega_{TO} = 167.5 \text{ cm}^{-1}$ (RT, [3]) then Ω_{SO} of 198 cm^{-1} calculated for spherical CdSe QD is close to measured Ω_{SO} . For a ZnS shell of 0.5 ML, the LO band shifts to the high-energy side by 1.9 cm^{-1} , becomes narrower and symmetric (Fig. 1b). Simultaneously, the intensity and energy of the SO-line is decreased. The quantity of Zn and S atoms in the cap layer is not enough to create a full ZnS layer, but enough to fill the broken bonds of Cd and Se surface atoms. Most likely, the core surface changes its morphology: the near surface layer becomes more ordered and number of near the surface stacking faults became essentially smaller. Then the surface tension force became stronger and the LO phonon energy shifts to the higher energy. Increasing the ZnS shell up to 2.2 ML (Fig. 1c) does not lead to a shift of the LO-band or a change of its width; this supports the assumption that reconstruction of the QD surface comes, probably, to an end at a ZnS thickness between 0.5 ML and 2.2 ML. Meanwhile the SO-band continues to shift to the lower energy (194.5 cm^{-1}) and increases in intensity. For a ZnS thickness of 3.4 ML (Fig. 1d), the LO and SO phonon energies remain approximately the same although the LO-phonon band becomes broader and the intensity of the SO-phonon line increases. The fact that the energies of the LO and SO phonons become unchanged at the ZnS thickness above 2ML indicates that the core/shell phonon parameters are almost established at this thickness. We speculate that the observed changes of the Raman spectra come from an increase of the intensity and a decrease of the energy of the mode with the ZnS shell thickness. Indeed, the energy and intensity of the SO modes of the core/shell structures depends on the value of the shell dielectric function (ε_M), which is in turn shell-thickness-dependent. Of course, it is

questionable if we can describe an ultra-thin ZnS layer by a macroscopic parameter ε_M . However, it is intuitively clear that growth of the ZnS shell will be followed by that of ε_M from its value corresponding to air up to some definite macroscopic value related to ZnS that results in modifications of the SO mode parameters. Importantly, the calculated dielectric constant of hexagonal ZnS ($\varepsilon_M = 8.48$, RT [3]) is about 180 cm^{-1} , that differs from Ω_{SO} of 192 cm^{-1} measured by us. The fact follows that the ZnS shell is probably amorphous rather than crystalline.

Finally, at a ZnS thickness of $\sim 2\text{ML}$ the surface of the CdSe core is mainly defect free although the structure of the shell is not established yet. It occurs at the thickness more than 3.4 ML where the shell is, most likely, amorphous. It is interesting to note that peak of the PL quantum yield of the analogous CdSe/ZnS quantum dots has been observed at a ZnS thickness in the range of 1.7 ML [1]. Probably, the defect-free core shell interface is more important for getting highly-luminescent QD structures than the increase of the shell thickness.

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NON-LINEAR OPTICAL PROPERTIES OF IV-VI SEMICONDUCTOR QUANTUM DOTS

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Transient differential absorption spectra, relaxation of bleaching-induced absorption, intensity-dependent transmission for PbS and PbSe quantum dots under strong quantum confinement are studied.

1 Introduction

It is known that in nanocrystals (quantum dots - QDs) strong quantum-confinement effects are observed, which in their turn lead to a large energy shift of the first absorption resonance with respect to the bulk band gap E_g . Variation of the nanocrystal size changes the spectral range of nonlinear response. The large bulk exciton Bohr radius (tens of nm) in IV-VI semiconductors allows strong quantum-confinement with relatively large nanocrystals. Narrow size distribution and low surface to volume ratio can be obtained for them. This means that study of IV-VI QDs gives opportunity to find out their properties in the strong quantum confinement regime with small surface effects.

2 Samples preparation and characterization

The phosphate glass samples were synthesized by a conventional batch-melting technique using P_2O_5 - Na_2O - ZnO - AlF_3 - Ga_2O_3 batch and PbS or PbSe modifier. Our silicate glass samples were prepared with a SiO_2 - Al_2O_3 - NaF - Na_2O - ZnO system at the semiconductor concentration of 0.4–0.6 mol. %. The size distribution of nanoparticles in the glasses of the both types was 6–10%. Fig. 1 presents the absorption spectra of PbS- and PbSe-doped glasses.

3 Kinetics of bleaching relaxation

The differential absorption ΔOD of p1 sample between the pump ($\lambda=1.08\text{ }\mu\text{m}$) and the probe ($\lambda=1.3\text{ }\mu\text{m}$) beams is presented in Fig. 2. It is defined as $\Delta OD=-\lg(T/T_0)$, where T_0 and T are the transmission of the probe beam without and with pump beam present, respectively. All the samples demonstrate the transient bleaching with a two-component decay. Moreover, time constants of relaxation are QD size dependent. The experimental data are fitted within the framework of the two-exponential decay model:

$$-\Delta OD = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \tag{1}$$

where A_1 , A_2 , τ_1 and τ_2 are the amplitudes and relaxation times of the faster and the slower bleaching relaxation components. Table 1 summarizes bleaching decay measurements. The fast component is attributed to the direct recombination of charge carriers and slow component is associated with the relaxation through trap states.

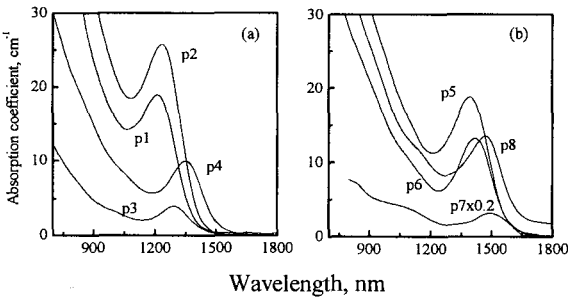


Figure 1. Absorption spectra of PbS- (p1-p7) and PbSe- (p8) doped glasses.

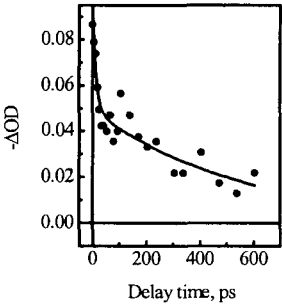


Figure 2. Bleaching relaxation of PbS-doped glass; dots – experiment, line – the best fit.

Table 1. The summary of bleaching decay measurements for the PbS-doped phosphate glasses with mean diameters D of nanocrystals. α_B is the background absorption of the samples; α_0 is the absorption coefficient at the excitonic maxima (for the rest notations see the text).

D , nm	λ_i , nm	τ_1 , ps	τ_2 , ns	A_2/A_1	α_B , cm ⁻¹	α_B/α_0
4.7	1210	15±5	0.6±0.1	1.17	1.0	0.04
4.8	1230	20±5	1.1±0.3	0.74	0.8	0.02
5.1	1290	25±5	>>1	0.02	0.1	0.02
5.4	1350	40±10		0.24	0.1	0.01
5.6	1400	90±10		0.29	1.0	0.04
5.8	1420	95±15		0.38	1.8	0.09

4 Intensity-dependent transmission

Intensity-dependent transmissions are measured at the wavelengths corresponding to the lowest and highest energy transitions. Fig. 3 presents results of measurements for the wavelengths of 1.08 and 1.54 μm (sample p7 from Fig. 1). Experimental data are analyzed in the framework of the fast-relaxing saturable absorber:

$$\alpha(I_0) = \frac{\alpha_0 - \alpha_B}{1 + I_0 / I_S} + \alpha_B \quad (1)$$

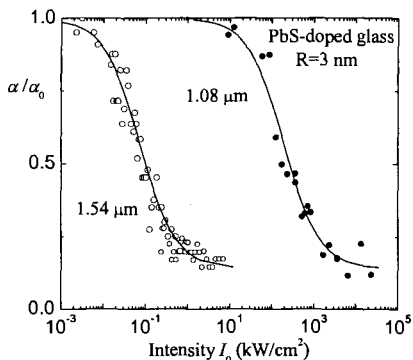


Figure 3. Relative absorption coefficient versus pump light intensity for PbS-doped glass. Dots - experimental data, lines – the best fit within the framework of fast –relaxing saturable absorber.

Results of measurements show that the saturation intensity I_s is much more for high-energy transitions (180 MW/cm^2 at $1.08 \mu\text{m}$ and 70 kW/cm^2 at $1.54 \mu\text{m}$). This can be explained by very short times of excitation relaxation for these transitions (1-2 ps [1]) in comparison with times τ_1 presented in Table 1.

5 Differential absorption spectra

Differential absorption spectra (DAS) under excitation of high-energy transitions are studied. The pump is done by 15-ps pulses from passively mode-locked Nd:YAlO₃ laser ($\lambda=1.08 \mu\text{m}$). White-light continuum generated from D₂O by a part of 15-ps laser pulse is used as a probe. Fig. 4 demonstrates DAS registered for sample p8 (see Fig. 1). The dots present values of differential absorption obtained from intensity-dependent transmission measurements for this glass at $1.08 \mu\text{m}$ and $1.54 \mu\text{m}$.

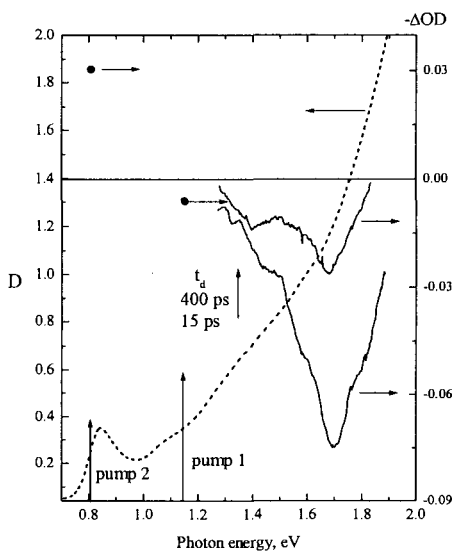


Figure 4. Linear (dashed line) and differential (solid lines) absorption spectra for PbSe-doped phosphate glass. See text for details.

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SYNCHROTRON INVESTIGATIONS OF ELECTRON-ENERGY SPECTRA IN III-V NANOSTRUCTURES

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With the use of synchrotron radiation X-ray near-absorption edge spectra in the range of P $L_{2,3}$ -edges were obtained for the first time in the following objects: InP quantum dots grown on GaAs <100> substrates by vapor-phase epitaxy from organometallic compounds and porous layers of InP obtained by pulse anodic electrochemical etching of single-crystalline InP <100> plates. These spectra represent local partial density of states in the conduction band. All nanostructures demonstrate quantum-size effects as an appearance of additional level at 3.3 eV from the bottom of the conduction band as well as dependence of the band gap in the investigated materials on these effects. Assumptions are made on the band-to-band origin of luminescence spectra in the studied nanostructures.

1 Introduction

Recently, III-V quantum-size structures draw serious attention of researchers due to their unusual properties. Formation of self-organized low-dimension semiconductor layers is of interest for researchers due to possibility of creating three-dimensional (3D) electron confinement in the uniform and coherent (non-dislocation) clusters. Unlike nano-size heterostructures formed under the use of complex photolithographic techniques, self-organized heterostructures obtained by molecular beam epitaxy (MBE) and MOC-hydride epitaxy (vapor-phase epitaxy from metallo-organic compounds) are characterized by a high density of states due to three-dimensional quantization, atomic-like structure of electron energy levels in the valence and conduction bands and high radiation efficiency due to small density of defects [1]. Porous quantum-size III-V materials can be used as matrices for obtaining of nanoscale quantum-wires.

The main idea of our study was to show the efficiency of synchrotron investigation for III-V materials with nanostructures. We investigated electron energy structure of unoccupied electron states in nanostructures with InP quantum dots buried in InGaP matrix grown on GaAs substrates and porous InP.

2 Experimental

X-ray absorption near edge structure (XANES) investigations were made at the Russian-German beamline of BESSY synchrotron radiation facility. Energy resolution was of 0.03 eV. Ultrasoft X-ray emission spectra (USXES) were obtained with X-ray laboratory spectrometer-monochromator RSM-500 with the energy resolution of 0.3 eV in the range of P $L_{2,3}$ -spectra. The depth of analysis in both cases was about 10-20 nm.

Nanostructures with quantum dots of InP were grown by vapor phase epitaxy from metal-organic compounds with Epiquip VP 50-RP. Self-organized nano-sized InP clusters were grown in $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ matrix on GaAs $\langle 100 \rangle$ substrate [2]. The structures contained InP nanocrystalline layer and its effective thickness varied from 3 to 10 monolayers. Nanocrystalline layer was capped with wide-band layer of $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ of 20 nm thickness.

Porous InP layers was prepared by pulse anodic electrochemical etching of single-crystalline n-InP $\langle 100 \rangle$ substrates in electrolytes containing F, Cl or Br ions.

3 Results and discussion

3.1 III-V nanostructures with InP quantum dots

P $L_{2,3}$ XANES of III-V nanostructures with InP quantum dots, grown on monocrystalline GaAs $\langle 100 \rangle$, and $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ alloy are presented in Fig. 1 (left). XANES represent the local partial density of unoccupied electron states in the conduction band (E_c is the bottom of the conduction band).

P $L_{2,3}$ USXES of $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ alloy presented in Fig. 1 (right) give the local partial density of occupied states in the valence band of the investigated material (E_v is the valence band top).

To date nobody could observe X-ray absorption edges in single-crystalline III-V compounds. Unlike crystalline GaP and InP, P $L_{2,3}$ electron yield spectra for nanostructures with InP quantum dots as well as the spectrum of $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ alloy are characterized by clearly observed fine structure with two main peaks at ~ 131 and 132 eV.

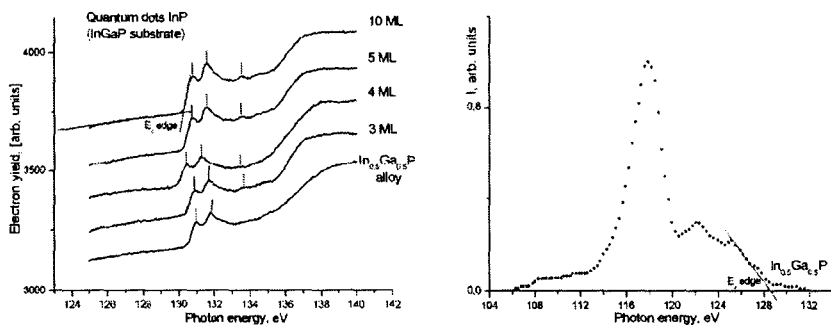


Figure 1. P $L_{2,3}$ XANES of nanostructures with InP quantum dots with different number of monolayers, E_c is the bottom of conduction band (left) and P $L_{2,3}$ USXES of $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ alloy, E_v is the valence band top (right).

All spectra have similar energy position of its features. The main difference of nanostructures with quantum dots XANES from $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ alloy one is the appearance of weak additional peak at the energy of 133.5 eV in spite of 20-nm $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ film protecting InP quantum dots. Its intensity increases with the increase of the number of InP monolayers from 3 to 10. Appearance of the additional peak at ~ 133.5 eV is connected with stresses at the border of InP quantum dots spreading through all $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ layer.

Comparison of the energy gap ~ 1.9 eV for $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ determined as the difference between the valence band top and the bottom of the conduction band with the energy of the photoluminescence peak demonstrates rather good accordance [2]. For InP quantum dots one can observe a decrease in conduction band bottom energy by the value ~ 0.2 eV that results in reducing of the band gap in these nanostructures.

3.2 Porous III-V phosphides

P $L_{2,3}$ XANES of porous InP grown on monocrystalline InP $\langle 100 \rangle$ by pulse anodic electrochemical etching of substrates in electrolytes containing HF, HCl or HBr are presented in Fig. 2 (left). USXES spectra of por-InP etched in HCl ambient is presented in Fig. 2 (right) together with those for monocrystalline InP.

The observed fine structure in XANES of por-InP coincides by the energy of peaks with that in XANES of quantum dots. However, the peaks of por-InP obtained by etching in HCl are very narrow which assumes formation of clusters or quasimolecules of InP in a porous layer. Cl ions are known to have rather high chemical activity relative to InP crystals.

USXES investigations of por-InP have shown that the main peak of P $L_{2,3}$ spectra representing the density of P3s-states in por-InP is by $\sim 25\%$ broader than in crystalline indium phosphide.

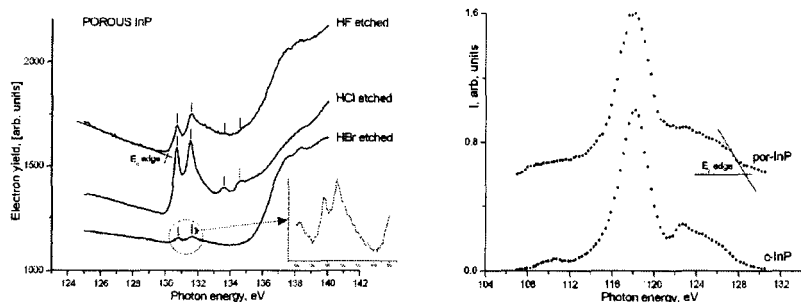


Figure 2. P $L_{2,3}$ XANES of porous InP etched in different electrolytes, E_c is the bottom of conduction band (left). P $L_{2,3}$ USXES of porous InP etched in HCl and c-InP, E_v is the valence band top (right).

4 Conclusions

- For the first time electron yield spectra near P $L_{2,3}$ -edge were obtained in nanostructures with InP quantum dots and in $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ alloys. XANES and USXES data are in a good agreement with photoluminescence spectra.
- X-ray absorption fine structure with two distinguished peaks is observed for all of the samples. This is connected with spin-orbit splitting of P $L_{2,3}$ - levels. The additional peak at ~ 133.5 eV is most likely due to quantum-size effect.
- Electron yield spectra of porous InP demonstrate narrow peaks of quasi-molecular character. Note that the peak at ~ 133.5 eV coincides with additional peak in XANES of InP quantum dots. This peak is well distinguished because of quasi-molecular character of bonds in por-InP.

Acknowledgement

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LUMINESCENCE OF Ge/Si QUANTUM DOTS SUBJECTED TO RADIATION DAMAGE AND HYDROGEN PASSIVATION

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Influence of proton irradiation and hydrogen passivation on the photoluminescence (PL) of MBE grown Ge/Si quantum dots (QDs) has been studied. An enhanced resistance of the QDs against irradiation as compared to the quantum wells and bulk silicon has been found. The passivation improves the thermal stability of the QD luminescence whereas the irradiation reduces it. Various carrier/exciton redistribution processes among the PL centers and the influence of defects have been observed.

1 Introduction and experimental

The study of the influence of defects on optical properties of Ge/Si quantum dots (QD) is of great importance for the future use of QD based devices. Recently, an enhanced hardness of the In(Ga)As/GaAs QD structures against particle irradiation as compared to bulk and 2D counterparts has been found [1-3]. No information exists so far on the radiation hardness of the Ge/Si QDs. In this paper we present the influence of the proton irradiation and hydrogen passivation on the photoluminescence (PL) of MBE grown Ge/Si QDs. An enhanced radiation resistance of the QDs as compared to the 2D wetting layer and bulk Si is shown.

The samples were grown by MBE at 700°C (for details see [4]). The samples had 10 layers containing quantum dots. For the irradiation with 2.4 MeV protons at RT, a Van de Graaff accelerator was used. The passivation with atomic hydrogen at ~250°C for 30 min was undertaken in a CVD reactor. The PL measurements were performed at a Bruker IFS 66v FTIR spectrometer equipped with a Ge detector. The samples were placed in a helium gas flow cryostat at temperatures from 5-300K. For the excitation in a wide power range we used the 488 nm line of an Ar⁺ laser.

2 Results and discussion

The PL spectra of the as-grown and passivated samples are shown in Fig. 1. The intense broad emission at 6000-7750 cm⁻¹ arises mainly from the QDs. The spectra of the as-grown and the passivated samples can be consistently fitted considering two pairs of bands (A and B in Fig. 2) along with two other single bands (E and D).

Each pair (A and B) is considered as a no-phonon (NP) transition and its TO phonon replica. The pairs are supposed to originate from two subsets of dots.

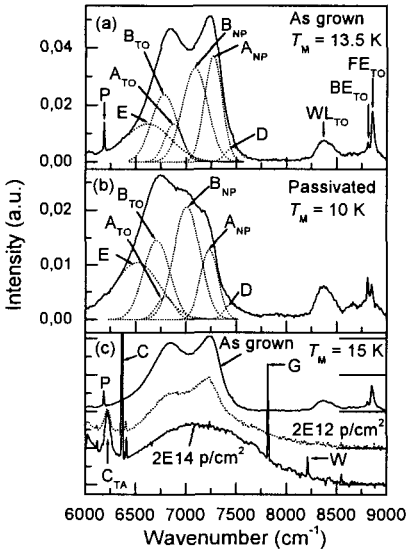


Figure 1. PL of the as-grown (a) and passivated (b) samples and corresponding fittings with Gaussian components. (c) PL of the samples prior to and after irradiation with the maximum and the minimum doses. The indices TO and LO label corresponding phonon replica. FE are free excitons, BE are excitons bound to shallow impurities in the Si substrate. WL is the wetting layer luminescence.

The origin of the D and E bands is unknown. Moreover, the spectra of as-grown samples contain the P-line due to a radiation-induced defect characteristic of elevated irradiation or annealing temperatures [5, 6]. This means that the samples during the growth are subjected to a particle bombardment.

The atomic hydrogen treatment removes the P line and enhances the overall PL intensity. This indicates a passivation of defect-induced deep levels that function as non-radiative recombination centers [7].

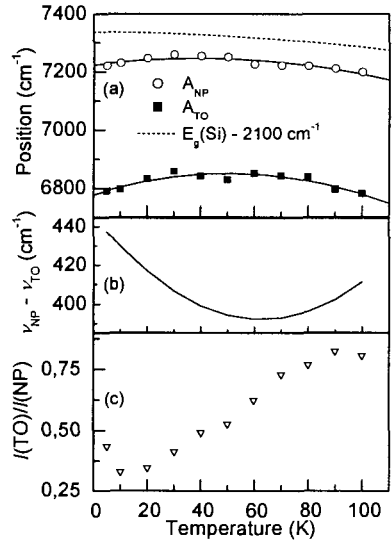


Figure 2. Temperature dependences, for the passivated sample, of (a) positions of the NP and TO components of the A dot emission and corresponding quadratic fits. The behavior of the Si bandgap is shown for comparison; (b) difference between the fitted curves for both components; (c) intensity ratio of the TO and NP components.

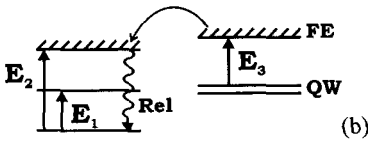
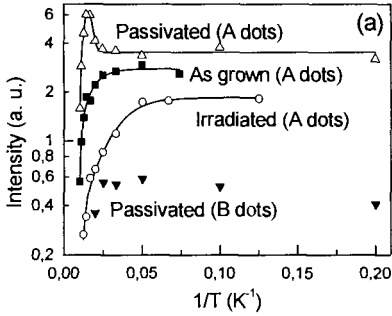


Figure 3. (a) Temperature dependences of the intensity of the A and B dot PL in the as-grown, passivated and irradiated ($2 \times 10^{12} \text{ p/cm}^2$) samples. The curves have been vertically shifted to avoid superposition of the points. (b) The level scheme used in the curve fitting.

and the broad band of defect origin are observed. The spectra of the dots irradiated to low doses can be separated from the defect spectra by subtracting the spectrum of this heavily irradiated sample normalized to the intensity of a distinct feature, e.g., of the C-line (Fig. 3c).

With increasing temperature, the NP-TO separation first increases, probably due to the thermal excitation of excitons/carriers in the dots into higher-lying states with a stronger leakage of the electron wavefunction into the Ge islands. However, at $T > 60\text{K}$ it starts to increase again. The TO/NP intensity ratio increases with temperature in accordance with the well-known models [8].

The dependences of the total intensities of the A dot luminescence have been fitted using the level scheme shown in Fig. 3b which can be described as:

$$\frac{I(T)}{I_0} = \left\{ \left[1 + c_1 \exp\left(-\frac{E_1}{kT}\right) + c_2 T^{\frac{3}{2}} \exp\left(-\frac{E_2}{kT}\right) \right] \left[1 + \frac{g}{1 + c_3 \sqrt{T} \exp\left(-\frac{E_3}{kT}\right)} \right] \right\}^{-1} \quad (1)$$

The first square bracket reflects the Maxwell-Boltzmann distribution of excitons in the dots. The term in the second square brackets describes the exciton supply from an external center [5]. The density of states in the dots is modeled by an excited level and a continuum of excited states which is a reasonable approximation taking into account the spectrum of excited states calculated in [9]. The carrier supply is

Upon irradiation, on the contrary to the passivation treatment, the protons penetrate far behind the QD layer and do not exhibit any passivation effect. In contrast, the irradiation, producing a uniform defect concentration up to the depth of several $10 \mu\text{m}$, reduces the intensities of all spectral components mentioned above, but to a different extent. So, it almost removes the B dots from the spectrum. Besides, the irradiation introduces well-known point defects with sharp NP lines (C, G and W) [5, 6] and a very broad band, also of defect origin. It is seen in Fig. 1 (c) for the lowest dose that the PL from the WL and bulk Si disappears whereas the PL from the QDs persists. This behavior clearly proves a higher radiation resistance of the dots as compared to the quantum wells and bulk material. At the highest dose ($2 \times 10^{14} \text{ p/cm}^2$) the QD PL is quenched too, and only sharp NP lines

thought as evaporation of free excitons from a QW with their subsequent capture by the dots. The fitting parameters are represented in Table 1.

Table 1. Activation energies obtained from the fitting of Eq. 1 to the data of Fig. 3a.

	As grown	Passivated	Irradiated
E_1 (meV)	13	45	8
E_2 (meV)	90	87	56
E_3 (meV)	–	57	–

For the passivated sample, a clear carrier supply to the A dots is observed. The corresponding activation energy E_3 is very close to the energy separation between the WL_{TO} and the FE_{TO} peaks in the PL spectrum. Beside the WL, another source of carriers can be the B dots because their spectra are thermally quenched at temperatures corresponding to the rise of the A dot intensity. In this case, thermally assisted tunneling between the dots could be responsible for the effect. No intensity increase is observed for the as-grown and irradiated samples, probably due to the capture of the released carriers/excitons by deep level defects. The coincidence of the E_2 values for the as-grown and the passivated samples is remarkably good. The E_2 value for the irradiated sample is too low, probably owing to some uncertainties due to the subtraction of the spectra.

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RAMAN SCATTERING OF ZEOLITES UNDER LOW-INTENSE VISIBLE EXCITATION: ROLE OF REDUCED Cu CLUSTER INCORPORATED IN ZEOLITES PORES

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Samples of natural zeolite, clinoptilolite, both with and without pore-incorporated Cu clusters were investigated by Raman spectroscopy and Diffuse Reflectance Spectroscopy (DRS). The reduction of Cu cluster incorporated in zeolite pores was carried out by heating of samples in dry H₂ flow at temperatures from 150 to 450°C for 4 hrs. The comparison of Raman and DRS spectra of all samples evidences the essential role of incorporated in pores and reduced Cu clusters for registration of zeolites Raman spectra under low-intensive (mW/cm²) visible excitation. Possible chemical enhancement mechanisms of Raman scattering cross section for SiO atomic groups in close proximity to self-assembling Cu clusters are discussed.

1 Introduction

Spatial heterogeneity and low reproducibility of surface roughness of the first generation of substrates for the surface-enhanced Raman spectroscopy (SERS) were the basic restrictions of the quantitative description of effect and comparative analysis of data obtained in different laboratories. For this reason SERS spectroscopy, despite of high selectivity and sensitivity, has not got wide application as a routine analytical technique in physical, chemical and biomedical laboratories.

The aim of this work is testing of SERS-activity of metal-containing microporous aluminosilicates or zeolites. Porous structure of zeolite skeletons caused by coupling of tetrahedral [SiO₄] and [AlO₄] building units is a unique basis for stabilization of a super-lattice of mono-dispersed metal clusters. Zeolite matrices combine the factors of nanoporosity and nanometer-scale chemical reactivity with respect to incorporated foreign ions, clusters, and nanoparticles [1].

2 Experimental

Natural clinoptilolite originates from Caimanes deposit (Moa, Cuba). We denote these samples as blank Cli. Copper ion exchange was carried out from 0.1 M

$\text{Cu}(\text{NO}_3)_2$ aqueous solution for one day. The samples were filtered, washed and dried under ambient conditions. We denote the samples obtained at this stage as CuCli. For the reduction of Cu, heating in a dry H_2 flow at temperatures from 150 to 450 °C for 4 hrs was carried out. We denote the samples obtained after such a procedure as $\text{Cu}^{\text{red}}\text{Cli}$. The copper content in the samples was determined by atomic absorption spectrometry. Diffuse reflectance spectra (DRS) were collected on a Varian Cary 300 spectrophotometer.

The Raman spectra were recorded with a DFS-52 (LOMO, St.-Petersburg) spectrometer. The ion Ar laser ILA-120 (488 and 514 nm) was used as a source of excitation. The excitation output of several mW/cm^2 on a sample was used as typical in SERS measurements. Differential Raman spectrum of $\text{Cu}^{\text{red}}\text{Cli}$ sample was obtained by subtraction signals of this and CuCli samples, after preliminary correction on fluorescence background. Pure fluorescence background spectra were registered for untreated and treated in hot hydrogen Cli samples.

3 Results and discussion

A pronounced maximum at 600 nm appears in DRS spectra of $\text{Cu}^{\text{red}}\text{Cli}$ at the H_2 flow temperature of 150°C (Fig. 1). Under intermediate reduction temperatures (e.g. 250 and 350°C) the initial oxidized Cu^{2+} form is still observed as a long wavelength shoulder near the main maximum at 600 nm. The DRS spectrum corresponding to the highest reduction temperatures (450°C) already does not contain the noticeable long-wave band. That evidences the complete reduction of Cu(II) under these conditions. The assignment of the absorption band at 560-600 nm in DRS spectra of three types of zeolites to plasmon resonance excited in copper nanoparticles was made in [2] using Mie simulation. It was shown that the observed DRS spectra of $\text{Cu}^{\text{red}}\text{Cli}$ agree very well with the simulated one for Cu nanoparticles of few nanometers in size. This fact allows to suggest that metal reduction process as a sequence of rather trivial processes ($\text{Cu}^{2+} + \text{H}_2 \rightarrow \{\text{Cu}^+ \text{ or } \text{Cu}^0\} + \text{H}^+$; $\text{Cu}^+ + \text{H}_2 \rightarrow \text{Cu}^0 + \text{H}^+$) in zeolite pores under hot H_2 flow may be accompanied by self-assembling of copper to nanosize clusters.

In a Fig. 2 the Raman spectra of CuCli and $\text{Cu}^{\text{red}}\text{Cli}$ samples are presented. The wide unstructured band (*a* in Fig. 2) is caused by fluorescence of organic molecules adsorbed on a zeolite surface from ambient atmosphere. The presence of this band is typical for all samples which have been not annealed in hydrogen. Such annealing promotes the release of water and organic fluorophores and results in significant decrease of a fluorescent background in Raman spectra (Fig. 2*b*). The weak but well-defined in the differential spectrum (Fig. 2*c*) vibrational bands, marked in this figure, appear only for Cu-containing samples and always after hot hydrogen processing. Thus, a necessary condition of these weak bands registration is the presence of the *reduced* Cu clusters in zeolites.

The bands marked in Fig. 2 can be attributed to vibrations of Si-O atomic groups of zeolite matrix. Thus, the vibrations at 1090 and 927 cm^{-1} are assigned to

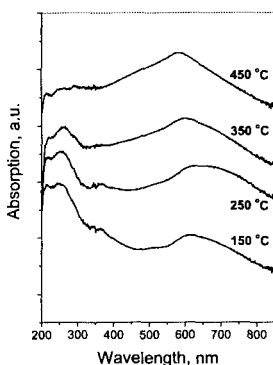


Figure 1. Evaluated from DRS, absorption spectra of Cu^{red}ClI samples, treated in H₂ flow at different temperatures (marked near the corresponding spectrum).

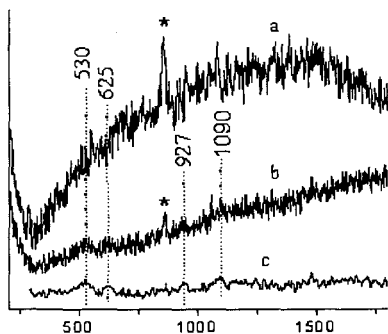


Figure 2. Raman spectra of CuClI (a), Cu^{red}ClI (b) samples and its differential Raman spectrum (c). Asterisks indicate tool line.

intense antisymmetric stretch vibrations of Si-O tetrahedra; the band at 625 cm⁻¹ is assigned to symmetric stretch vibrations of Si-O bonds or to vibrations of zeolite framework rings. The band at 530 cm⁻¹ can be assigned to deformational vibrations of Si-O bonds.

Heating of Cu-exchanged zeolites in H₂ flow leads to reduction of copper in zeolites pores and this process is very likely accompanied by self-assembling of metal atoms to clusters of few nanometers in size. The formation of such clusters is confirmed by DRS. The possible indirect evidence of Cu cluster formation is the appearance of weak vibrational bands of strongly heterogeneous and large (in molecular scale) objects - zeolite framework- with probable SERS-active clusters inside it. In this context, zeolites represent rather interesting basis for development of “chemical” enhancement model of Raman scattering in close proximity to the isolated nanometer-size metal clusters.

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SURFACE PLASMON RESONANCES AND LIGHT SELECTION IN METAL-DIELECTRIC NANOSTRUCTURES OF VARIOUS SPATIAL ARRANGEMENT

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Tunable light selection over a spectral range of surface plasmon resonances has been theoretically and experimentally studied for metal-dielectric nanocomposites of various spatial arrangement: random close-packed (**I**), polycrystalline quasiregular (**II**) planar structures and 1D-photonic crystals consisted of a metal nanoparticle stratified array (**III**). It was shown for structures **I** and **II** that main parameters of surface plasmon resonances are dependent on the lateral electrodynamic coupling determined presumably by nearest ordering into a metal nanoparticle array. It was revealed for structure **III** that within the plasmon-polariton resonance the selective suppression/increase of extinction is caused by subwavelength periodicity (the joint electron and photon confinement). Tuning ways are proposed for control of the hybrid attenuation band parameters in the structures under study.

1 Introduction

Collective optical excitations, like surface plasmon-polaritons in partially-ordered metal nanoparticle arrays, tend to be spatially localized. The localization facilitates a giant increase of linear and nonlinear optical responses such as Raman scattering, enhancement of spontaneous emission rate, nonlinear absorption and refraction. In this paper the spectral manifestation of light localization into metal-dielectric nanocomposites is studied in the visible. The effect of the lateral electrodynamic coupling on transmission/reflection optical spectra is investigated for planar silver nanoparticle arrays (random close-packed and polycrystalline quasiregular structures). Combined action of electron and photon confinements is demonstrated experimentally and considered theoretically for 1D-photonic crystals consisted of a metal nanoparticle stratified array.

2 Method

The considerable distinctions between optical spectra of a metal nanostructure and corresponding bulk metal appear due to surface modes (plasmon-polariton resonances) in nanoparticles and size dependence of their optical constants. In the case of partially-ordered nanoparticle arrays these effects are of the collective nature because of strong electrodynamic coupling. The theoretical approach for regarding

these coherent interactions is the statistical theory of multiple wave scattering (STMWS). In the present paper, simulations for planar nanostructures were made in the quasicrystalline approximation (QCA) of STMWS [1]. Size-dependent optical constants were calculated using the model of the electron mean free path limitation [2]. For layer-periodic nanostructures the QCA was complemented by the self-consistent procedure to estimate electrodynamic coupling between different monolayers within the stack.

In the frame of QCA the particle space ordering is described by the radial distribution function $g(R)$. For random close-packed structures with short-range ordering we used the solid sphere approximation [1]. For the polycrystalline arrays the ordering scale is limited by the domain boundaries and characterized by the correlation length L_C . At the greater distances we can suppose the homogeneous distribution of particles:

$$g(R) = \begin{cases} \frac{4\eta}{\pi d^2} \cdot \sum_i \frac{C_i}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{(R-L_i)^2}{2\sigma_i^2}\right), & \text{for } R \leq L_C \\ 1, & \text{for } R > L_C \end{cases}$$

The position L_i of i -th peak for $g(R)$ coincides with the radius of corresponding coordination sphere and determined by the lattice type. Its half-width σ_i is determined by the loose disturbance of a real particle system and corresponds to a possible small deviation of the particle location from the lattice site. C_i is the coefficient determined by the ordinary normalization conditions for the radial distribution function.

3 Results and discussion

To study particle correlation effects in the plasmon resonance absorption in the visible we have firstly compared the spectral characteristics of silver nanoparticles monolayers at the various particle surface concentrations n_0 (Fig. 1). The monolayer overlap parameter $\eta = n_0 \pi d^2 / 4$ was equal to 0.4 for the particle diameter of 3.5 nm. These values were close to parameters of the structures fabricated by the thermal evaporation technique. A comparison of experimental and calculated data allows concluding that the enhancement of collective coherent interactions with particle concentration growth transforms a structure of plasmon resonances and influences their spectral position. The red shift of the plasmon resonance with packing factor increasing is a consequence of the lateral coupling growth.

The difference between transmission spectra of random close-packed and polycrystalline quasiregular planar arrays with the equal surface concentration of particles (Fig. 2) shows an appearance of multiplex structure and global extinction suppression for a polycrystalline array compared to the close-packed one. A

comparison of two polycrystalline arrays with different scales of ordering proves that the main features of their spectra are determined by the nearest ordering.

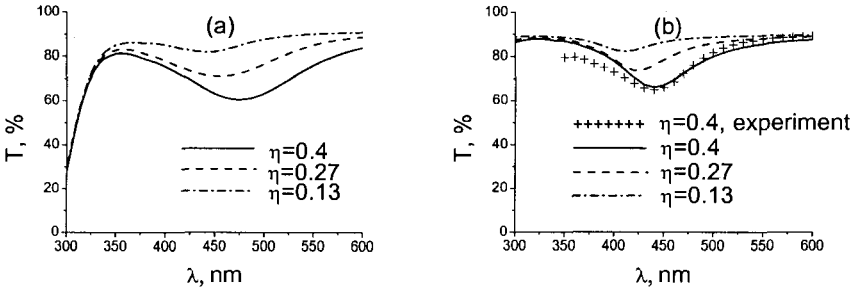


Figure 1. Transmission spectra for a monolayer of silver nanoparticles ($d=3.5$ nm) supported by glass substrate at different particle surface concentrations: (a) monolayers are deposited on the dielectric film ($n=1.5$), experimental data; (b) monolayers are embedded into the dielectric film, cross-line corresponds to the experimental data, all others depict the calculated data.

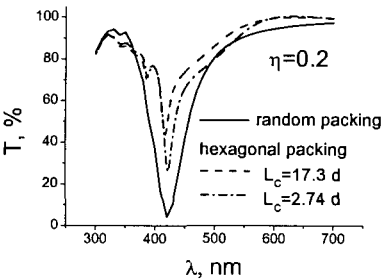


Figure 2. Spectral dependence of transmittance for Ag nanosphere monolayer in KCl ($d=35$ nm, $\eta=0.2$) on type of particle arrangement - random packing and polycrystalline hexagonal array at different sizes of an arrayed domain L_C .

To demonstrate the influence of longitudinal coherent interactions we have investigated the transmission and reflection spectra of 1D photonic crystals based on close-packed silver nanosphere monolayers separated by thin solid dielectric films. The strongest spectral manifestation of longitudinal electrodynamic coupling was shown [2] to take place in the case of joint electron and photonic confinements. In order to achieve it we chose intermonolayer film thicknesses l_M so that the photonic band gap and the metal nanoparticle surface plasmon band could be realized at close frequencies in the visible.

The separating layer optical thicknesses were fixed (Fig. 3) about $\lambda_0/4$ or $\lambda_0/2$, where λ_0 corresponds to the plasmon absorption maximum of a metallic nanoparticle monolayer in the KCl environment. These multilayer structures were fabricated by the thermal evaporation technique followed by deposition of metal and dielectric materials without breaking the vacuum between the evaporation steps. The structures grown by this technique are realized as a sequence of Ag island films separated by KCl intermediate layers of a subwavelength thickness. These data

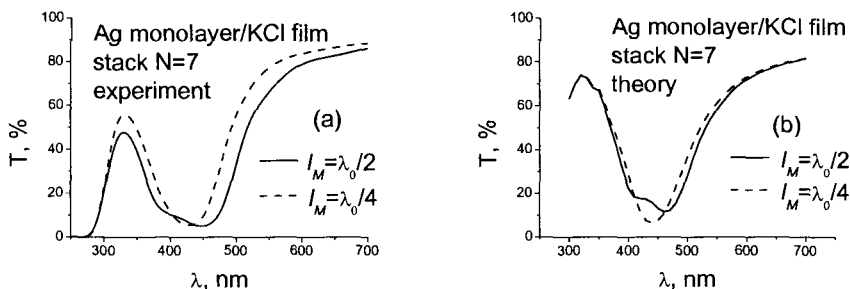


Figure 3. Transmission spectra for a stack of Ag nanoparticle monolayers (layer number $N=7$, $d=3.5$ nm, $\eta=0.4$) separated by KCl films at their different thickness l_M : (a) experimental data; (b) calculated data.

demonstrate that one-dimensional ordering results in control of the interaction between light and metal nanoparticles. It is a powerful tool for optical spectra tuning in the vicinity of the surface plasmon resonance. For example, doublet structure of the attenuation band is clearly seen for $l_M \sim \lambda_0/2$. In a common case the special choice of periodicity parameters allows to suppress or increase transmission, reflection and absorbance of metal nanoparticle arrays over a wide spectral range.

Acknowledgements

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OPTICAL NONLINEARITY OF COPPER NANOPARTICLES SYNTHESIZED BY ION IMPLANTATION IN SILICATE GLASS

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Copper nanoparticles have been synthesized in silica by 50 keV Cu^+ ion implantation with doses of 8.0×10^{16} ion/cm². Nanoparticles were characterized by a absorption band of surface plasmon resonance in the visible range. Metal nanoparticle composite glasses were analyzed by the Z-scan method at the IR wavelength of Nd:YAG laser radiation 1064 nm. The third order nonlinear susceptibility in the analyzed medium with simultaneous nonlinear refraction and absorption were considered as complex values. It is suggested that the samples with nonlinear absorption is perspective ones for optical applications.

1 Introduction

Composite materials formed by nanometer-sized metal particles embedded in dielectrics have a growing interest owing to the large values of fast optical Kerr susceptibility, $\chi^{(3)}$, whose real part is related to the intensity-dependent refractive index n_2 [1]. Ion implantation has been shown to produce a high density of metal nanoparticles (MN) in glasses [2]. The high-precipitate volume fraction and small size of MN leads to giant value of the $\chi^{(3)}$ [3]. This stimulates an interest in the use of ion implantation to fabricate nonlinear optical materials.

The most conspicuous manifestation of confinement in the optical properties of MN is the surface plasmon resonance (SPR) that strongly enhances their linear and nonlinear responses around SPR wavelength [4]. Therefore, the impact of dielectric confinement on the nonlinear optical response of MN has been generally studied using different techniques of wavelength scale in the vicinity of SPR, typically, in the visible range with noble MN [1]. However, for optical applications it is important to have an enhanced nonlinearity of composite materials at a specific wavelength. Here we concentrated on the study of nonlinear optical properties at 1064 nm of silica glasses with Cu nanoparticles formed by ion implantation.

2 Method

Silica glasses from Heraeus were implanted with Cu^+ ions at 50 keV, to a dose of 8.0×10^{16} ion/cm² at a beam current density of 10 $\mu\text{A}/\text{cm}^2$. A crucial condition of the implants is that they are thermally bonded to a water cooled sample holder and maintained at a constant substrate temperature of 20°C during the implantation.

The samples were analyzed by the small-angle x-ray scattering technique under grazing incidence (GISAXS) [3]. Optical transmittance spectra were measured from 300 to 900 nm using a dual beam Perkin Elmer Lambda 19 spectrophotometer. For nonlinear experiments, the Z-scan technique was applied [5]. The mode-locked Nd:YAG laser which generated picosecond pulse train was used. Single pulse (35 ps) from the train was amplified up to 1 mJ at $\lambda=1064$ nm. The radiation intensity 10^{10} W/cm² was lower than the threshold of optical damage (6×10^{10} W/cm²) of the analyzing sample. Experimental set-up with closed aperture allowed to determine the sign and magnitude of n_2 and $\chi^{(3)}$. For measurements of nonlinear absorption coefficient, β , the experimental set-up with open aperture was used. For calculations of n_2 , $\chi^{(3)}$ and β of the samples equations of the Z-scan theory were applied [5].

3 Results and discussion

At a dose higher than 4×10^{15} ion/cm² the metal-ion concentration exceeds the solubility limit for silica and causes the growth of Cu nanoparticles [2]. The size distribution of metal nanoparticles in dielectrics in the depth are not symmetrical. For silica implanted at higher doses the larger metal nanoparticles will be formed close to the sample surface, whereas smaller particles will be deeper (up to 50 nm) in the substrate.

The GISAXS data displays a centrosymmetric shape of the scattering intensity distribution, indicating that the Cu nanoparticles are spherical with an average diameter of ~ 4 nm, in consistense with a quite narrow size distribution. Transmittance spectrum has maximum near 565 nm that also gives evidence for presence of the Cu nanoparticles in the glasses.

The characteristic of normalized transmittance of the implanted glasses $T(z)$ in a closed-aperture scheme is shown in Fig. 1. The glass with Cu nanoparticles has a negative sine of n_2 showing a self-defocusing nonlinear process. The calculated n_2 is presented in Table 1. There were no changes in $T(z)$ curves for SiO_2 , therefore, the optical nonlinearity in implanted glass is stimulated by MN.

Nonlinear refraction of the composite materials results from different mechanisms such as the Kerr effect and thermal focusing [5]. Taking into account that the laser intensity and repetition rate were large enough, the speed of MN hyperpolarizability causing Kerr-induced self-defocusing should overlap the thermal focusing mechanism.

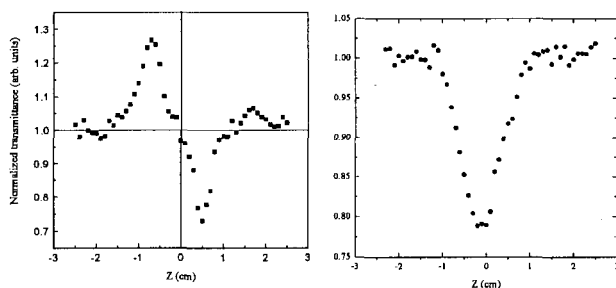


Figure 1. Normalized transmittance spectra (closed aperture scheme – left) and (open aperture scheme – right) of implanted glasses: SiO₂:Cu.

Nonlinear absorption measurements of the samples have shown that nonlinear absorption took place only in the glasses with MN. Fig. 1 shows decreasing of $T(z)$ at the focal point in an open-aperture scheme that demonstrates strong nonlinear absorbance. Calculated values of $\chi^{(3)}$, $\text{Re}\chi^{(3)}$ and $\text{Im}\chi^{(3)}$ are presented in Table 1.

Table 1. Nonlinear parameters of implanted glasses: SiO₂:Cu at 1064 nm.

n_2 $\times 10^{-9}$ esu	β $\times 10^{-7}$ cm W ⁻¹	$\text{Re}\chi^{(3)}$ $\times 10^{-9}$ esu	$\text{Im}\chi^{(3)}$ $\times 10^{-10}$ esu	$ \chi ^{(3)}$ $\times 10^{-10}$ esu
-16.47	10.8	-3.86	7.83	37.8

Materials with the nonlinear absorption, as in our case, are of great interest because of their use as optical limiters [1]. On the basis of preliminarily simulations using β of the optical limiting process it was determined the values of 15-fold limiting for the laser intensity close to the threshold 6×10^{10} W/cm² of optical sample damage for SiO₂:Cu. This result leads to a conclusion about applicability of glasses with implanted MN in optical limiting at $\lambda=1064$ nm.

Acknowledgements

We are grateful to the Alexander von Humboldt Foundation and RFBR 00-15-96615 for financial support of A. L. S. The co-authors of NPO “Academprigor” acknowledge the partial support of the Scientific and Technology Centre in Ukraine under agreement Uzd-29.

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THE OPTICAL RESPONSE OF SILVER ISLAND FILMS EMBEDDED IN FLUORIDE AND OXIDE OPTICAL MATERIALS

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The optical behaviour of silver island films embedded in optical thin film materials has been studied by spectrophotometry. The silver cluster surface plasmon absorption line position and width strongly depend on deposition temperature and ambient material. Electron micrographs of the samples allow to establish the correlation between silver cluster geometry and optical behaviour. The first results of Rigorous Coupled Wave Approximation (RCWA) calculations reproduce the spectrophotometric experimental results.

1 Introduction

Optical thin films are widely used today for a tremendous variety of applications. In many cases, the desired film specifications (for example a high transmittance or a high reflectance over a certain wavelength range) are achieved utilizing constructive and destructive interference of light beams that are multiply reflected at the thin film interfaces, so that one has to use film materials with an extinction coefficient as low as possible (ideally zero) [1]. There is another situation in the case of selective absorber coatings. Their function is to supply a high absorptance in a well-defined wavelength range, while there shall be negligible absorption in other spectral regions. For such coatings, one needs materials with high extinction coefficients at the relevant wavelength.

Our approach to the absorber design makes use of the optical excitation of surface plasmons in small metal particles. In general, the free electron portion in metals is responsible for the typical brightness of metallic surfaces. The situation is quite different in small metal particles with a size of only a few nanometers. Here motion of the previously “free” electrons is confined inside a particle, so that electrons behave optically in a similar manner like bound electrons – they show resonant absorption behaviour and are therefore a natural choice for a selective absorber material.

The key point is that the resonance wavelength of the surface plasmon excitation depends on a variety of parameters, such as size and shape of the particles as well as their arrangement and the dielectric properties of their environment [2,3]. One may therefore manipulate the optical behaviour of metal particle assemblies in order to prepare materials with tailored optical absorption properties. The purpose

of this paper is to report on the optical properties of silver particles embedded in ultrathin films of various fluoride and oxide optical thin film materials.

2 Experimental

The samples have been prepared by e-beam evaporation of a dielectric layer followed by thermal evaporation of the silver fraction, which builds the island film, while the sandwich is completed by a further dielectric film. In every sample, intentionally the same amount of silver (corresponding to an average thickness of 4 nm, as recorded by quartz monitoring) has been embedded in a 6 nm thick dielectric film, formed from either MgF_2 , LaF_3 , SiO_2 , or Al_2O_3 . The optical transmittance T and reflectance R of all films have been measured by a Perkin Elmer Lambda 19 spectrophotometer. To correlate the optical properties with the sample morphology, transmission electron microscopy (TEM) has been applied.

3 Results

Fig. 1 shows the measured optical loss $L = 1 - T - R$ for samples, where the silver islands are embedded in SiO_2 . The samples differ in their deposition temperature which has a tremendous effect on their optical properties. The loss peak of silver particles shifts to the blue with increasing deposition temperature.

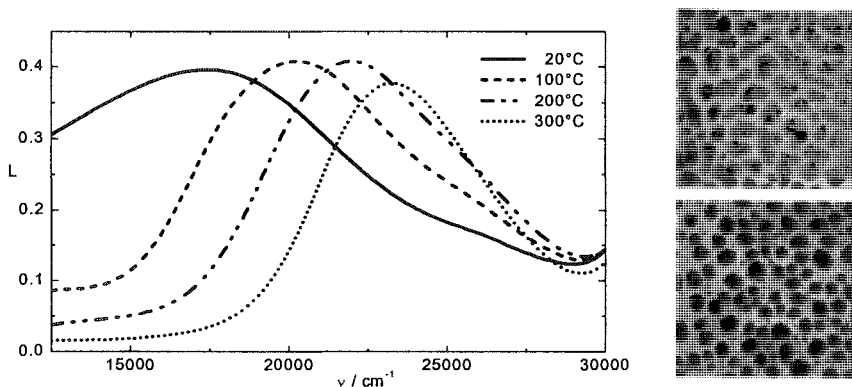


Figure 1. Left: The measured optical loss L of samples, where silver clusters are embedded in SiO_2 . An increase in deposition temperature leads to a blue-shift of the surface plasmon absorption maximum. Right: TEM image of the 20°C (top) and 300°C (bottom) samples. Area 175 nm x 175 nm. The silver islands appear as dark spots.

In order to quantify the experimental results, the following spectral moments have been calculated for every sample (ν is the wavenumber):

$$\delta\nu = \sqrt{\frac{1}{L_0} \int_{\nu_{\min}}^{\nu_{\max}} L(\nu) (\nu - \langle \nu \rangle)^2 d\nu}; \quad \langle \nu \rangle = \frac{1}{L_0} \int_{\nu_{\min}}^{\nu_{\max}} L(\nu) \nu d\nu; \quad L_0 = \int_{\nu_{\min}}^{\nu_{\max}} L(\nu) d\nu.$$

The calculated spectral moments are presented in Table 1. $\langle \nu \rangle$ tends to increase with increasing wavenumber, while $\delta\nu$ decreases. This behaviour of the samples is caused by a different morphology of the embedded silver islands. Fig. 1 also shows examples of TEM-results. At low deposition temperatures, the islands are rather irregular in shape (top), while they become more spherical with increasing deposition temperature (bottom). Due to the small lateral dimensions of the clusters and intercluster distances, we assume that the observed optical loss is mainly due to absorption, and not due to scattering.

Table 1. Spectral moments as determined from experimental data.

Host material	Deposition temperature °C	$\nu_{\min}$ 1/cm	$\nu_{\max}$ 1/cm	L_0 1/cm	$\langle \nu \rangle$ 1/cm	$\delta\nu$ 1/cm
MgF ₂	20	12500	30000	4900	19600	4500
	100			4100	21300	4200
	200			3100	23200	3700
	300			1750	24950	3000
LaF ₃	20	12500	30000	4600	19200	4300
	100			4100	21000	3800
	200			2700	21150	4200
	300			1650	23550	2900
SiO ₂	20	12500	30000	4700	19400	4400
	100			4100	21200	3900
	200			3550	22450	3500
	300			2700	23450	3000
Al ₂ O ₃	20	4000	29000	5400	14150	6700
	100			6000	15700	6000
	200			5300	17300	5400
	300			4700	18250	4900

4 Discussion

Let us start with a qualitative understanding of the main optical effects. Clearly, in non-spherical silver islands (as mainly occurring at low deposition temperatures), the plasmon excitation may be accomplished along different axes of the cluster. Excitations parallel to the longer axis of a prolate cluster lead to light absorption at

lower frequencies, which causes both the red-shift (shift of $\langle \nu \rangle$) and the broadening (increase in $\delta \nu$) of the resulting absorption line of statistical non-spherical cluster assemblies when compared to spheres.

A rigorous method to calculate the optical loss of periodic planar cluster assemblies is offered by RCWA (Rigorous Coupled Wave Approximation) calculations commercially available in grating solver software [4]. In order to apply this method to the calculation of the optical response of planar silver cluster assemblies such as shown in Fig.1, one has to assume that the cluster arrangement is periodically continued in two dimensions. In practice, we assumed a 300 nm x 300 nm broad “elementary cell” which contains 55 silver islands of 7.8 nm height (Fig.2).

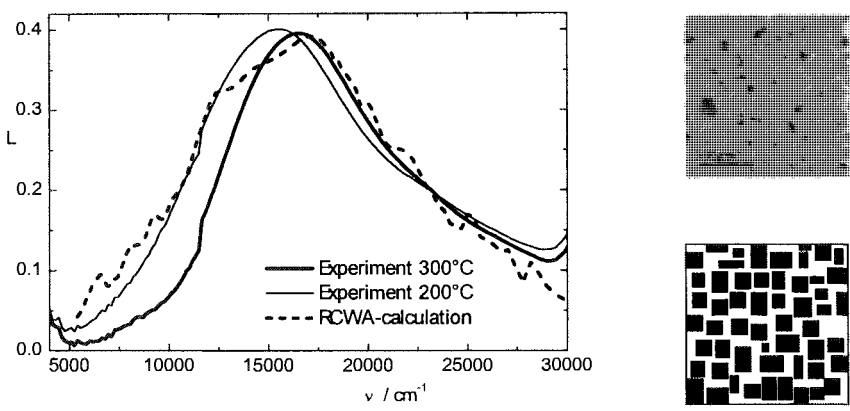


Figure 2. Left: The optical loss L of the samples, where the silver clusters are embedded in Al_2O_3 . Solid Line: measured; Dash: RCWA-calculation. Right: TEM image of the sample (top) and assumed island geometry in the RCWA-calculation (bottom). Area 300 nm x 300 nm. The silver islands appear as dark spots.

Fig. 2 also shows the result of the calculation of the optical loss of such a silver cluster arrangement embedded in Al_2O_3 , compared to the corresponding experimental loss of samples which have been deposited at 200°C and 300°C. There is a good qualitative agreement in the graphs, and the theoretically calculated spectral moments ($L_0 = 5400 \text{ cm}^{-1}$, $\langle \nu \rangle = 17000 \text{ cm}^{-1}$, $\delta \nu = 5400 \text{ cm}^{-1}$) are consistent with the corresponding experimental data from the table.

In summary, we state that the silver cluster absorption line may be controlled by typical thin film deposition parameters. This is particularly important for incorporation of such island films into “classical” interference coating designs. Moreover, the observed absorption is particularly strong. In our experiments, we achieved extinction coefficients as large as 4.0 – for comparison, typical organic dye crystals like phthalocyanines have extinction coefficients in the visible range of about 1. Perspectively, these ultrathin metal-dielectric-composite films will be

incorporated into multilayer stacks to design thin film systems with tailored absorption and reflection behaviour.

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PROPERTIES OF NANO-SIZED PARTICLES FORMED DURING DOUBLE-PULSE LASER ABLATION IN LIQUIDS

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Pulsed laser ablation of metal samples in liquid environments by combination (in coincidence or in sequence) of two laser beams at different wavelengths has been examined in order to clarify a possibility of formation of size-selected metal nanoparticles. It has been shown that dual laser ablation technique in transparent liquids is suitable for fabrication of nanoparticles of metals where the size of particles can be controlled. The mean diameter of silver particles fabricated in water was typically in the range of 15-20 nm.

1 Introduction

Last years considerable efforts have been directed to preparation of metal nanoparticles having a desired diameter and shape. A number of production techniques has been reported such as wet chemical processes, (co-precipitation, complexation, sol-gel), physical vapor deposition, sputtering, and laser ablation methods [1]. The ultimate goal of each technique is fabrication of monodisperse structures with a predetermined size, shape and arrangement.

Recently, the fabrication of nanoparticles under laser ablation of solid samples has become the focus of many studies [2,3]. The laser ablation experiments are typically carried out in gas or vacuum environments. The processes of laser ablation in liquids have been much less investigated [4]. But the feasibility of laser ablation in transparent liquids for nanoparticle synthesis has been recently demonstrated. [5,6].

In this paper we demonstrate capabilities of double-pulse laser ablation (DPLA) in liquid environment for fabrication of metallic nanoparticles with a narrow size-distribution. We examined optical properties of the silver colloidal solutions prepared by DPLA in order to reveal the role of the second laser pulse in a size change of the particles produced in the ablation plume.

2 Experimental

Experiments were made by using a double pulse Nd:YAG³⁺ laser system (1064 nm, repetition rate – 10 Hz, pulse duration – 10 ns, energy – 45 mJ in each pulse) or two

10 Hz pulsed Nd:YAG lasers, operating at 1064 nm (IR) and 532 nm (green), each with 40 mJ pulse in a 5-mm beam.

The laser beams were focused on the surface of the metallic samples (Ag, Cu) placed in the cell with liquid (water). The laser beams were employed for ablation both singly and together with appropriate temporal delays between pulses. The power density at the target was in the range of 10^8 - 10^9 W/cm².

Spectroscopic characterization of the ablated plume was performed by the time resolved emission spectroscopy. The review emission spectra from plasma were recorded in the UV and visible ranges with a CCD array detector.

The formed water-suspended particles were analyzed by optical absorption spectroscopy and transmission electron microscopy (TEM). A 1-cm-pathlength-quartz cell was used for the absorption measurements with a UV-visible double-beam spectrophotometer. The preparation of samples for the electron microscopy was carried out by the following procedure. A drop of the colloidal solution was placed on a copper grid coated with an amorphous carbon film, which was then dried in a desiccator.

3 Results and discussion

The properties of metal colloids fabricated by laser ablation were studied by recording their extinction spectra as a function of preparation conditions. Typical extinction spectra of the colloids are shown in Figs. 1,2. The spectra exhibit characteristic absorption bands with peaks (located around 400 nm for silver colloidal particles). These bands are related to the collective excitation of conduction electrons (surface plasmon resonances). The shape and intensity of the plasmon band in the absorption spectrum depend on the regime (double-pulse or single pulse) of laser processing. By using the double pulse laser ablation and the same exposure time, the efficiency of ablation was greater and the band in the absorption spectrum was more intense (curve 2 in Fig. 1). The silver colloids prepared by double pulse laser ablation exhibited a blue shift in the absorption maximum. The blue shift in the absorption maximum was accompanied by narrowing of the surface plasmon band. In addition, the band became more symmetrical without red tailing. On the contrary, the plasmon resonance bands of silver colloids prepared by single pulse laser ablation were broadened to the red spectral region. The presence of tailing toward the red indicates broader distribution of particle shapes and sizes, and perhaps the presence of aggregates. The blue shift band and an increase in the magnitude of absorption is indicative of a decrease in particle diameter. So, the second laser beam creates smaller particles.

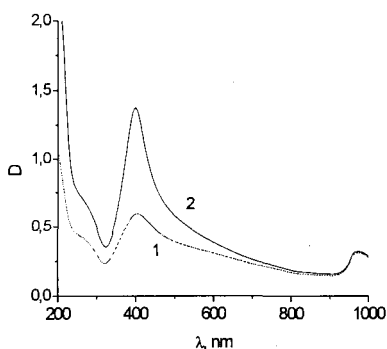


Figure 1. Optical absorption spectra of Ag colloidal solutions produced by the repetitive (10 Hz) single-pulse 1064 nm (1) and double-pulse (1064 nm + 1064 nm, 7 μ s pulse separation) laser ablation (2) of silver target in water.

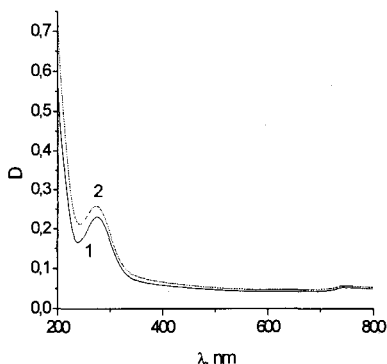


Figure 2. Optical absorption spectra of Cu colloids prepared by the repetitive single-pulse 1064 nm (1) and double-pulse (1064 nm + 1064 nm) laser ablation (2) of copper target in water. Pulse separation in double-pulse regime – 7 μ s.

The mechanism of the laser-induced fragmentation is not fully explored yet, although heating, (which causes melting and vaporization) as a result of the strong absorption of the laser energy by the particles and disintegration of the parent particles into smaller ones because of the charging under laser-pulse excitation will be suggested for discussion.

The spectral features of copper colloids prepared by laser ablation in water (Fig. 2) in the UV region around 275 nm can be assigned to the metal interband transitions and, perhaps, because copper is reactive to produce some compounds such as copper oxide and hydroxide. Owing to the high reactivity of copper, it was practically impossible to observe the copper plasmon band near 560 nm [5].

The absorption spectra of spherical particles of colloidal dimensions can be calculated by Mie theory from a wavelength dependence of optical constants of the particles relative to the surrounding medium [7]. Spherical particles that do not interact with each other exhibit a single resonance as long as $r \ll \lambda$ is valid, where r and λ are the particle size and wavelength of the incident light, respectively. In this size regime the surface plasmon frequency is essentially size independent. Colloidal metallic particles produced by laser ablation have dimensions typically on the 3-20 nm range. Within this size range for spherical particles there is no strong dependence of the absorption spectra on the particle size. Nevertheless, the peak shift is expected to be observed in extinction spectrum when the size/shape distribution of the particles and their aggregation state are changed. For experimental colloids there are likely to be broadenings of the spectra due to polydispersity, partial aggregation or departures from the spherical particle shape.

Transmission electron microscopy of the Ag particles fabricated by laser ablation in distilled water indicates that the average size of the particles is 20 nm with an asymmetrical distribution of sizes ranging from approximately 15 to 45 nm. Detailed characterization of the colloids by electron microscopy is currently in progress.

4 Conclusion

Laser ablation of metal targets in liquids provides a rapid and simple method for preparation of stable metal nanoparticles. Advantages of this technique include its versatility with respect to metals or solvents, and the absence of chemical reagents or ions in the final preparation. The developed technique offers a good control over the particles' formation process and an effective collection and conservation of fabricated materials.

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Mn PHOTOLUMINESCENCE KINETICS IN QUANTUM DOTS

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A description is proposed for luminescence decay in Mn-doped CdS quantum dots based on a model implying radiative and dispersive non-radiative decay of excited impurity ions. The model provides an adequate explanation of experimental photoluminescence kinetics in CdS:Mn nanocrystals. The excited state lifetime evaluated for Mn^{2+} ions is about 2.3 ms and close to the bulk case.

1 Introduction

In the recent years doped semiconductor nanocrystals are widely investigated including their intrinsic properties and the properties modified by impurities [1, 2]. Quantum confinement effects are well known to modify the electronic properties of nanocrystals when their diameter is comparable to or smaller than the diameter of the bulk exciton [1-3]. Moreover, early results on ZnS:Mn nanocrystals [4] show that the position of the Mn^{2+} emission band is slightly shifted from that of the bulk material. The authors of Ref. [4] also claimed that the ${}^4\text{T}_1$ level lifetime of manganese ions in nanocrystals reduced by five orders of magnitude as compared to the bulk material. However, recent reports do not confirm this statement [5]. Further studies of luminescence in doped nanocrystals are necessary.

In this paper, we present and test the model implying radiative and dispersive non-radiative decay of excited impurity ions to study the effects of energy transfer on optical properties (emission and lifetime) of CdS:Mn^{2+} semiconductor nanocrystals embedded in a polymer matrix.

2 Samples and experiment

The structures under investigation were prepared by sol-gel reactions in the form of thin 1-mercaptopropyltriethoxysilane films containing CdS:Mn^{2+} nanocrystals [6]. The mean radius of nanocrystals obtained from optical measurements using the results of tight-binding calculations was equal to 25 Å. Manganese concentration was determined using laser atomic-absorption analysis and the value of x for $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ was found to be 0.023.

The spectra of optical absorption and cw-photoluminescence (PL) are typical for small semiconductor nanoparticles under a strong quantum confinement effect.

The absorption edge shifts to the blue (Fig. 1). The photoluminescence has a broad band peaking at 640 nm. The luminescence line shape is not Lorentzian and has a strong Stokes shift. Photoluminescence excitation (PLE) spectra have revealed a fine substructure of the band at its short-wave wing whose origin is attributed to the intrinsic luminescence contribution and to radiative recombination on defects.

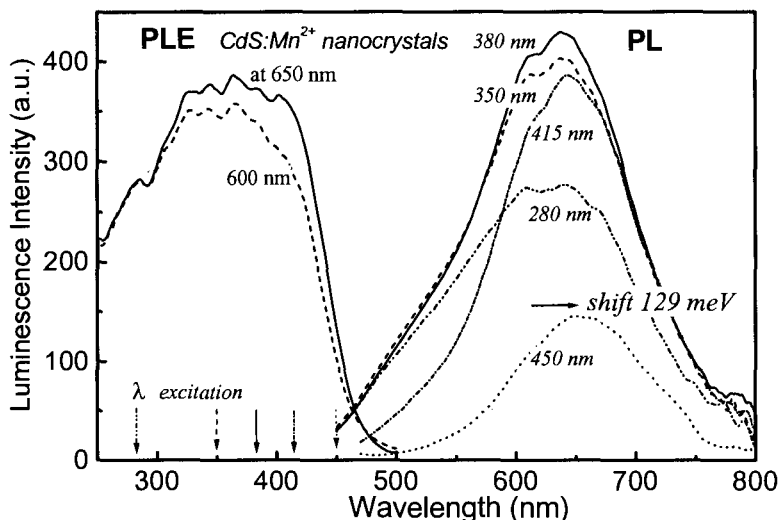


Figure 1. Photoluminescence emission spectra (PL) and photoluminescence excitation spectra (PLE) of CdS:Mn²⁺ nanocrystals embedded in a polymer film.

3 Photoluminescence kinetics

The PL kinetics at various wavelengths are non-exponential (Fig. 2). Decay behavior analysis reveals a weak long-decay component on a millisecond scale and an intense faster component on a submillisecond scale. Its relative contribution is increasing monotonously with increasing photon energy. The time-resolved PL spectra recovered from kinetics data have confirmed the existence of the fast decay component at the short-wave branch of the PL spectrum which cannot be ascribed to electronic transitions in a 3d-shell of Mn²⁺ ions.

We found that the account of possible energy transfer between the excited states of semiconductor nanocrystals and Mn²⁺ ions results in the satisfactory description of the PL decay by the function which reads

$$I(t) = I_0 \exp\{-t/\tau_0 - \alpha(t/\tau_0)^\beta\} + I_{dark},$$

where $\tau_0 = 2.3$ ms is the excited state lifetime, $\alpha = 2.93 \div 6.15$ is a parameter depending on the characteristic distance and concentration of excitation centers, and $\beta = 0.18 \div 0.22$ is a scaling factor determined by the fractal space dimension.

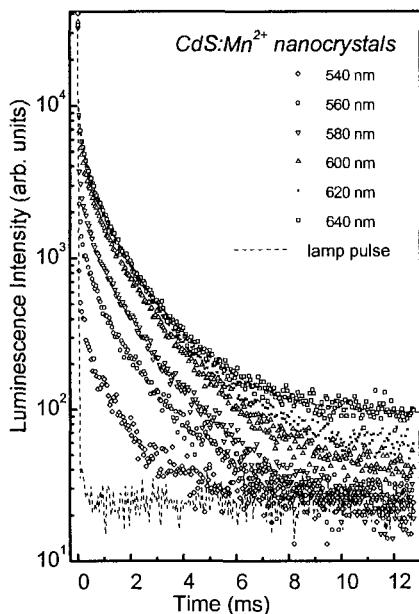


Figure 2. Photoluminescence kinetics of quantum size CdS:Mn²⁺ nanocrystals at various wavelengths.

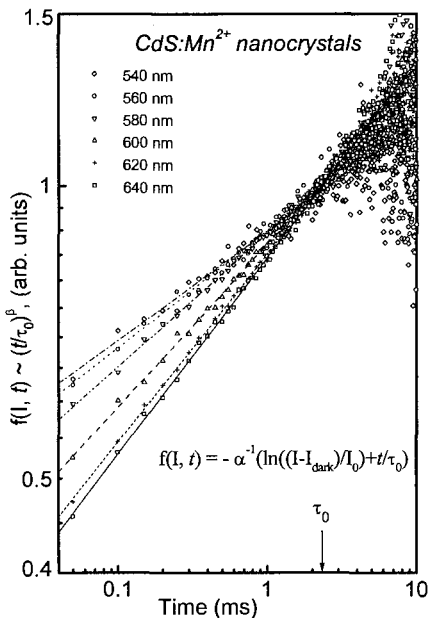


Figure 3. Fitting of Mn²⁺ photoluminescence kinetics data by the modified stretched exponential function.

For the special case of non-exponential PL kinetics in a porous matter the similar phenomenological model was proposed earlier for explaining PL kinetics of porous silicon by Gaponenko *et al.* [7]. The more perfect decay function can be obtained at the account of various ways of energy transfer and migration of charge. However it is clear that the τ_0 value revealed in our experiments (Fig. 3) exhibits no increase in the transition rate in nanocrystals doped with manganese as compared to bulk crystals and glasses contrary to the results reported by Bhargava *et al.* [4].

4 Conclusion

The optical properties of CdS:Mn nanocrystals contained in a sol-gel matrix are studied and more particularly the luminescence spectra and kinetics of the Mn²⁺ emission at room temperature are examined. The manganese emission in the

nanocrystals is the result of an energy transfer from the semiconductor nanocrystal to the manganese ions.

We found that the quantum confinement effect does not modify the emission lifetime inherent in bulk materials. Our results are at variance with those obtained by Bharghava *et al.* for ZnS:Mn nanocrystals and partially agree with recent results by Bol *et al.* [5] and Chamarro *et al.* [8].

Acknowledgements

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FIELD ENHANCEMENT NEAR THE ANNEALED NANOSTRUCTURED GOLD DETECTED BY OPTICAL SPECTROSCOPY WITH THE PROBE BIOMOLECULES

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Tailoring of spectral properties of vacuum deposited gold films with substrate annealing procedure allows to excite selectively the surface-enhanced Raman scattering (SERS) or the surface-enhanced fluorescence (SEF) of biomolecules without changing a light source. The phenomenon can be explained in the context of self-assembling of gold granules on sprayed film and tuning up the position of localized plasmon (LP) excitation band to the molecular absorption. The separation of molecules from nanostructured gold surface on long distances results in further increasing of surface-enhanced secondary emission. The long-range field enhancement is discussed as collective effect of several interacting gold islands. The possible geometry of probe disposition in "hot spots" on self-aggregated gold films is presented.

1 Introduction

Progress in technology of nanosized materials has renewed attention to surface-enhanced optical phenomena. The nanoscale metals, which have important applications in surface-enhanced Raman scattering (SERS) [1], surface-enhanced fluorescence (SEF) [2, 3] and optoelectronic nanodevices are of particular interest.

Very recently Bawendi and co-workers [4] reported about fivefold increase in the observed fluorescence intensity of single CdSe/ZnS nanocrystals (NCs) and striking reduction in their fluorescence blinking behavior due to interactions with a rough metal film. The distance-dependent enhancement and quenching of NC fluorescence has been observed by us using the layer-by-layer polyelectrolyte deposition technique to insert well-defined spacer between gold colloidal films and NCs [5] with maximum enhancement for the 9-layer spacer (≈ 11 nm in thickness).

The aim of this work is to study the observable near-field phenomena and, particularly, to establish the existence of an optimal distance at which probe

fluorescence intensity attains the maximum. Nonmonotonous distance dependence for SEF was discussed earlier [2, 3, 5] as a result of the two competing processes – long-range field enhancement and short-range fluorescence quenching. For the first time we present the similar dependence for SERS and SEF of the same dye separated by other monolayer deposition techniques from surface of the annealed thick gold films (TGFs).

2 Materials and methods

TGFs with mass thickness of 5-30 nm were fabricated by vacuum deposition of gold on quartz slides. They were annealed in air at different temperatures. The parameters of vacuum deposition and annealing were the same as previously described for silver films [6]. The deposition procedure of or Langmuir monolayers cadmium behenate (BC, Sigma) or poly-L-lysine (Sigma) on TGF was also reported earlier [3, 6].

1,4-Dihydroxy-5,8-bis-{{[2-(2-hydroxyethyl)-amino]ethyl} amino}-9,10-antracenedione dihydrochloride (mitoxantrone, mitox) was purchased from Sigma and deposited onto a reference blank quartz and TGF surface by soaking of the appropriate substrate in a 10^{-6} M dye aqueous solution for 20 min followed by rinsing with distilled water and drying in air.

AFM images of the Au colloidal film surface were recorded in air using a Nanotechnology P4 AFM/STM microscope. The Si_3N_4 cantilever tip used had a spring constant of 0.4 N/m. The tip was pyramidal with radius of 10 nm.

3 Results and discussion

Fig. 1 presents AFM image of TGF annealed at 240°C (TGF-240) (Fig. 1 a) and 340°C (TGF-340) (Fig. 1 b). The annealing at 240°C resulted in breaking up of the sprayed film and assembling superficial clusters and grains of gold in islets of a roughly conical shape with well separated one from another spherical top of approximately 5 nm in diameter. The higher annealing temperature resulted in growth of the height and lateral dimensions of the gold islets. The tenfold differences in island size and its surface distribution (Fig.1 a, b) result in the weak hypochromism and the low-wavelength shift of TGF-340 absorption band in comparison with TGF-240. This band corresponds to the localized plasmon (LP) resonance excitation in gold grains on TGF surface dipole-dipole interaction between them. As it was shown earlier [3], these two substrates assuming the were adapted by annealing pretreatment to selectively enhance one or another type of the secondary emission of the same molecule under the same excitation.

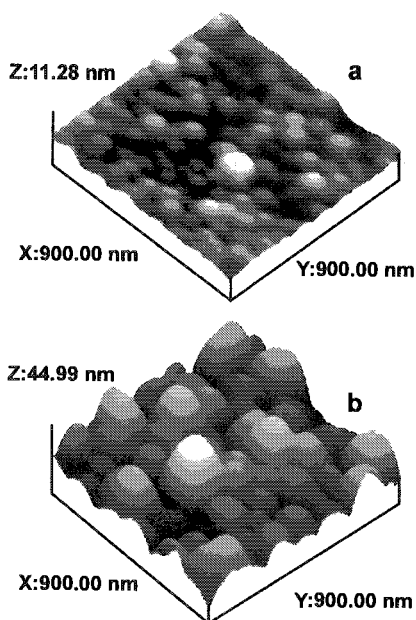


Figure 1. AFM-image of TGF-240 (a) and TGF-340 (b).

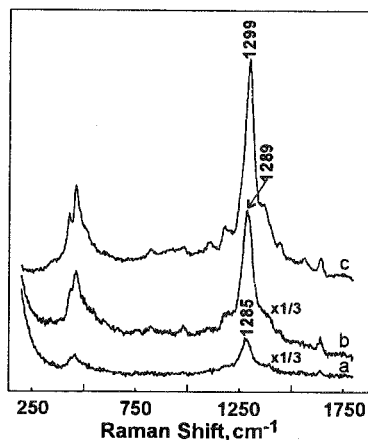


Figure 2. SERS spectra of mitox deposited on TGF-340, covered by 1 (a), 3 (b) and 5 (c) Langmuir layers of cadmium behenate.

The maximum of fluorescence enhancement factor per mitox molecule ($K_{fe} = 50$) was obtained for TGF-240 covered by physisorbed poly-L-lysine monolayer [3].

Fig. 2 shows the SERS spectra of mitox, deposited on TGF-340, covered by different number of BC Langmuir monolayers. The sharp increase of mitox SERS signal is observed as number of the BC layers increased. It is 10 times higher for 5 layers of separated spacer than for 1 layer (Fig. 2 a, c). Each BC molecule consists of 20 CH_2 -groups, and for five BC Langmuir layers this number is equal 100. Estimation gives the thickness of 1 and 5 layered BC spacer as 3 and 15 nm, correspondingly. Note that no fluorescence was detected with TGF-340 even if thickness of spacer is ca. 15 nm, that is enough to exclude possible chemical effects and quenching due to the Forster resonance energy transfer.

The more detailed treatment of the enhancement of Raman, resonance Raman scattering and fluorescence from molecules adsorbed on identical, well-characterised, silver-island films was made by Nitzan and co-workers [7]. They presented a unified picture of the electromagnetic interactions in these inelastic scattering processes and established that there is a hierarchy of the enhancement phenomena.

Our results concerning the increase of SERS with distance from surface of nanostructured gold surface are in good agreement with predictions by

O. J. F. Martin and co-workers [8] for the interacting plasmon resonant nanoparticles. The possible location of a molecular probe is some point between two or more islands on gold surface. We suppose that these points generate so called “hot spots” [9] on self-aggregated colloids that are exclusively active in SERS. The simple theoretical evaluations based on the field superposition near the dissipative medium are also in good agreement with the distance dependence obtained by us and the model of molecular probe location.

Acknowledgements

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PLANAR Cu NANOSTRUCTURE: EXPERIMENTAL AND THEORETICAL INTEGRAL LIGHT SCATTERING CHARACTERISTICS

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The subject of investigation is the planar structure comprising of oxidized Cu granules (5.5 nm in diameter) manufactured by laser electrodispersion. The spectra of coherent transmission, diffuse transmission and reflection were measured for these specimens. Experimental data were compared with those spectrum calculated with regard to some parameters of the planar structure and the size-dependence of Cu optical constants.

The keen interest in research of planar metal-containing nanostructures is due to peculiarities of its physico-chemical parameters compared with the corresponding parameters of bulk materials and, thus, due to great promise of these structures for nanoelectronics and optics. Recently revealed high conductivity of Cu nanostructures at room temperature stimulated an interest in scattering measurements as an alternative nondestructive statistical method to study properties of these nanoobjects. Such investigations must precede the costly near-field optical microscopy.

This work is an initial stage in optical investigations of planar nanostructures comprising of randomly electro-charged and non-charged Cu granules with oxide shell (as well as their chains and aggregates) deposited as a monolayer on a quartz substrate and covered with amorphous SiO₂ [1]. This stage includes the spectral measurements of direct transmission (with the detection angle of 15 minutes), diffuse transmission and reflection for a layer of Cu granules on a substrate and the calculation of monolayer transmission coefficient based on the single-scattering approach.

Experimental data were used to calculate the absorption spectrum of a monolayer, the effective scattering, absorption, and extinction coefficients. The optical properties of a single granule were theoretically obtained with Mie theory for the homogeneous and two-layered spheres with regard to size-dependence of Cu optical constants in the frame of the model of a mean free path electron limitation

[2]. Matrix (SiO_2), core (Cu) and shell (Cu_2O , CuO) optical constants had been taken from [3, 4]. Calculated values of transmission coefficients have been corrected on the real quartz substrate extinction. A comparison of experimental and theoretical results are presented in Fig. 1.

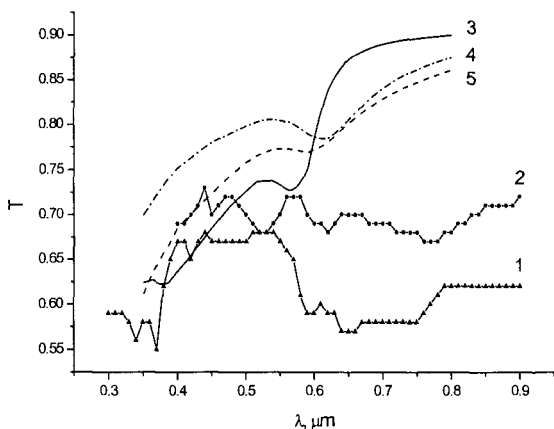


Figure 1. Spectral dependencies of transmission coefficients for a monolayer of surface oxidized Cu nanogranules with the diameter of 8 nm deposited on the quartz substrate. Curves 1, 2 correspond to the measured values of direct (T_{dir}) and diffuse (T_{diff}) transmission, respectively. Curves 3, 4, 5 depict calculated coherent transmission for a monolayer of homogeneous Cu spherical nanoparticles (3) and monolayers of two-layered particles with a Cu core covered with Cu_2O (4) or CuO (5) shell (shell thickness is 1 nm) surrounded by SiO_2 (20 nm). Relative surface concentration of particles is 0.72.

Positions of absorption bands in 570-610 nm range depend on presence of particle shell, on the granule surface concentration and optical properties of the substrate and matrix. The absorption bands situated in 200-570 nm range can be assigned to absorption by aggregates of several Cu atoms or CuO and Cu_2O molecules. The experimental and theoretical maxima of the monolayer absorption bands are in fairly good agreement. They correlate with the time of granule oxidation and, thus, with thickness of the oxide shell.

The extinction bands in near IR are likely stemming from absorption and scattering by chains of granules. Electron and atomic-force microscopic measurements revealed that the specimen was a monolayer of highly-packed individual spherical granules (64%) and chains from two (23%), three (9%) and four and more (4%) granules. These chains may be modeled in the first approximation as prolate spheroids. We use exact SVM approach [5] to calculate the scattering by such spheroids. The spectrum of transmission coefficient for above mixture of spheres and spheroids is depicted in Fig. 2. We neglected the size effect and oxide shells.

The observed quantitative disagreement between theoretical and experimental values of the direct transmission coefficient may be explained by ignoring the polydispersity and, more importantly, by neglect of concentrational nonlinear effects and surface correlations in granule positions.

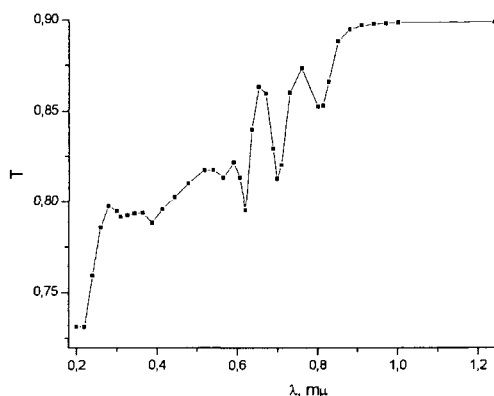


Figure 2. Calculated spectral dependence of coherent transmission coefficients for a monolayer of Cu nanogranules on a quartz substrate with regard to chains (individual granule diameter is 5.4 nm).

Interestingly enough that the maximum experimental value of the monolayer scattering coefficient takes place in the plasmon resonance region. This value is a mere half as absorption coefficient. The positions of extrema in luminescence spectrum correlate with maxima in the absorption spectrum.

The data obtained may be used to estimate the kinetics of granule oxidation in different technological conditions as well as to obtain qualitative information on presence of granule chains. Further experiments and theoretical calculations are necessary for quantitative estimations.

Acknowledgements

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HIGH-ORDER HARMONIC GENERATION BY CARBON NANOTUBES: DENSITY MATRIX APPROACH

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A rigorous quantum-mechanical description of the interaction of intense femtosecond laser pulses with single-wall carbon nanotubes has been presented. Quantum kinetic equations for the density matrix have been derived and solved numerically in the time domain. The influence of interband transitions on the high-order harmonics generation has been investigated.

1 Introduction

Carbon nanotubes (CNs) possess peculiar transport and optical properties. One can expect a especially pronounced manifestation of these peculiarities on exposing CNs by intense femtosecond laser pulse, which provides nonlinear interaction. In particular, the nonlinearity can lead to the high-order harmonic generation (HHG). This process is of interest for several reasons. First, this gives possibility to generate coherent ultrashort light pulses at very short wavelengths in the devices confined to a submillimeter region. Second, spectra of the harmonics provide us useful information on the transport and electron properties of CNs.

In the given paper we present a quantum-mechanical theory of HHG in CNs utilizing a single electron approximation in the tight-binding model. Our approach is based on the previous study HHG in CNs presented in Refs. [1,2] and allows us to incorporate into consideration direct interband transitions. We have calculated an axial current density, spectrum of which is responsible for HHG in CNs.

2 Theoretical basis

Let us consider an infinitely long rectilinear single-wall CN illuminated by an intense femtosecond pulse with the carrier frequency ω_0 . The z-axis is assumed to be directed along the axis of the CN. Let the pulse be incident normally to the CN

axis and polarized along it: $\mathbf{E}(\mathbf{r},t) = \mathbf{e}_z E_z(\mathbf{r},t)$. We restrict our consideration π -electrons, assuming that their motion in the hexagonal lattice can be described within the tight-binding approximation. Motion of the π -electrons in CN exposed to an external electromagnetic field is governed by the quantum kinetic equations for the density matrix ρ_{ab} :

$$\begin{aligned}\frac{\partial \rho}{\partial t} + e E_z \frac{\partial \rho}{\partial p_z} &= \frac{2e E_z}{\hbar} R_{ab} \Phi, \\ \frac{\partial F}{\partial t} + e E_z \frac{\partial F}{\partial p_z} &= \omega_{ab} \Phi, \\ \frac{\partial \Phi}{\partial t} + e E_z \frac{\partial \Phi}{\partial p_z} &= -\omega_{ab} F - \frac{e E_z}{\hbar} R_{ab} (2\rho - 1),\end{aligned}\tag{1}$$

where $\rho = \rho_{aa}$, $F = \text{Re} \rho_{ab}$, $\Phi = \text{Im} \rho_{ab}$, and ω_{ab} is the frequency of interband transitions. Since the intensities of high-order harmonics are smaller compared to the input intensity, we have neglected their influence on the electron motion. Relaxation terms have been excluded from the system (1). The reason for such simplification is small duration of pumping pulse as compared with the characteristic relaxation time in CNs.

Taking into account the hexagonal crystalline structure and transverse quantization of the first Brillouin zone, it can easily be obtained that in zigzag CN in the tight-binding approximation the dispersion law of π -electrons [3] and matrix elements R_{ab} are as follows:

$$\begin{aligned}\varepsilon(p_z, s) &= \gamma_0 \left[1 + 4 \cos\left(\frac{3b p_z}{2\hbar}\right) \cos\left(\frac{\pi s}{m}\right) + 4 \cos^2\left(\frac{\pi s}{m}\right) \right]^{1/2}, \\ R_{ab}(p_z, s) &= \frac{b \gamma_0^2}{2 \varepsilon^2(p_z, s)} \left[1 + \cos\left(\frac{3b p_z}{2\hbar}\right) \cos\left(\frac{\pi s}{m}\right) - 2 \cos^2\left(\frac{\pi s}{m}\right) \right],\end{aligned}\tag{2}$$

and $\omega_{ab}(p_z, s) = 2 \varepsilon(p_z, s) / \hbar$, $s = 1, \dots, m$. The current density induced in the CN by the incident electromagnetic field can be exposed to: $j_z = j_z^{(1)} + j_z^{(2)}$, where

$$\begin{aligned}j_z^{(1)} &= 2j_0 \sum_{s=1}^m \int \frac{\partial \tilde{\varepsilon}}{\partial p_z}(p_z, s) \rho(p_z, s) dp_z, \\ j_z^{(2)} &= 4 \frac{j_0}{\hbar} \sum_{s=1}^m \int \tilde{\varepsilon}(p_z, s) R_{ab}(p_z, s) \Phi(p_z, s) dp_z.\end{aligned}\tag{3}$$

$j_z^{(1,2)}$ are the current density related to intraband and interband transitions respectively, $j_0 = e \gamma_0 / \sqrt{3} \pi \hbar m b$, where $\gamma_0 = 3.03$ eV, $b = 1.42$ Å.

The system of differential equations (1) was solved numerically in the time domain. Initial conditions for (1) reflect the fact that π -electrons at room temperature are distributed accordingly to the Fermi equilibrium distribution with

zero electrochemical potential. Boundary conditions follow from the fact of periodicity of the density matrix elements $\rho_{aa,bb,ab}(t,p_z)$ at boundaries of the first Brillouin zone:

$$\rho|_{t=-\infty} = [1 + \exp(\varepsilon(p_z, s)/k_B T)]^{-1}, \quad F|_{t=-\infty} = 0, \quad \Phi|_{t=-\infty} = 0, \quad (4)$$

$$\rho(t, 2\pi\hbar/3b) = \rho(t, -2\pi\hbar/3b).$$

The similar expressions can be written for an armchair CN.

3 Numerical results and discussion

In this section we present some results of numerical simulation of interaction of an intense laser pulse with an isolated single-wall CN. The pumping pulse is assumed to be Gaussian: $E_z = E_z^0 \exp[-(t - t_0)^2 / \sigma^2] \sin(\omega_0 t + \phi_0)$, where ω_0 and $\Gamma = 2(\ln 2\sigma)^{1/2}$ are the pumping pulse carrier frequency and its FWHM. Numerical results are presented in Fig. 1. Parameter $\Lambda = 3ebE_0/2\hbar\omega_0 w_{cn}$ is used for characterization of the field intensity, $w_{cn}=1$ for armchair CNs, $w_{cn} = 3^{1/2}$ for zigzag

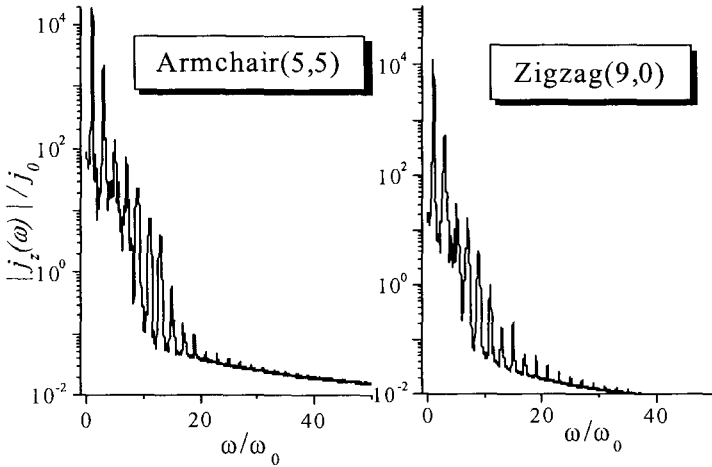


Figure 1. Amplitude spectrum of the induced current in armchair and zigzag CNs illuminated by the Titan-Sapphire laser pulse: $\Lambda=1$, $\sigma=4$, $\omega_0=\omega_{\text{Tisp}}$.

ones. Normalization coefficient j_0 for armchair CN can be obtained from that for zigzag one by multiplying the latter by $1/3^{1/2}$. In amplitude spectra of the current, the acute maxima appropriate to odd harmonics laser carrier frequency ω_0 are legibly visible. Absence of even harmonics is explained by the mirror reflection symmetry with respect to planes perpendicular to the axis of CNs and is in

agreement with Ref. [4]. Analogously to the result obtained in [1,2], Fig. 1 shows rapid decrease of the spectrum intensity with the harmonic number growth. Essential qualitative difference of the spectra obtained is the presence of continuous background. This results in the harmonics of higher order to become indistinguishable.

4 Conclusion

A quantum-mechanical theory of interaction of intense subpicosecond laser pulse with the single-wall CN has been presented in this paper. Spectrum of the induced current has been calculated. It represents the superposition of narrow discrete lines and continuous background. Presence of continuous background makes impossible to observe harmonics of the order higher than $N=25\div31$. Moreover, the interference of currents stimulated by inter- and intraband transitions lead to the reduction of the effectiveness of HHG in comparison with the semiclassical model [1,2].

There are several perspective directions of the development of the presented theory. First, indirect interband transitions of π -electrons should be included in the consideration; they give rise to the transverse current in CNs. Second, the HHG theory should be generalized for the case of multi-wall CNs or CN-composites. Third, effects of chirality should be taken into account.

Acknowledgements

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MECHANICAL PROPERTIES OF NANOSTRUCTURED AMORPHOUS CARBON-METAL FILMS

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The correlation of grain size of metal and size of carbon clusters with mechanical properties (hardness, friction, wear) of a-C:H,Cu and a-C,(Cu,Zr) films have been investigated.

1 Introduction

A considerable interest to study carbon and composite carbon-metal coatings deposited in vacuum is due to a possibility of widely changing the physical properties of coatings depending on the structure of carbon and metal clusters and elemental composition [1-3]. However, the role of grain size of metal and size of carbon clusters in properties of composite carbon-metal films is not established yet. The aim of the present work was to study the correlation of the structure, elemental composition, sp²/sp³-types carbon clusters ratio with mechanical properties for two types of carbon-metal coatings: a-C:H,Cu and a-C,(Cu, Zr).

2 Experimental

The hydrogen-free coatings a-C,(Cu,Zr) were formed on Si (100) substrates using cathodic arc vacuum deposition (CAVD) with high negative bias of 20 kV applied to the sample [4]. The thickness of coatings of all the types was ≈200 nm. a-C:H,Cu copper-carbon composite films were deposited on Si (100) substrates using a microwave PECVD process of carbon from Ar-CH₄ mixtures combined with sputter deposition of metal from a copper target [5]. The thickness of coatings was varied from 0.2 to 0.5 μm.

The composition was obtained from RBS measurements using α particles of 2 MeV or protons of 1 MeV depending on the film thickness. Mechanical testing was carried out using Nano Indenter II with Berkovich indenter. The load was varied in the range of 0.25-50 mN. The Raman scattering (RS) spectra of coatings were measured using Spex 1403 spectrometer under excitation by argon laser (488 nm) with the power on a sample of 0.3-0.35 W. The velocity of friction tests («pin-on-surface») was of 4 mm/s, the pin made of BK-8 hard alloy (87.5 HRC), the load was of 1N.

3 Results and discussion

For hydrogen-free a-C,(Cu, Zr) films obtained by CAVD method the depth distribution of Cu and Zr as was shown in [5] is inhomogeneous. The average depth concentration of Cu and Zr is 14-17 at.%.

Raman scattering spectra from a-C,(Cu,Zr) films and the results of their mathematical treatment are given in Fig. 1. and in Table 1.

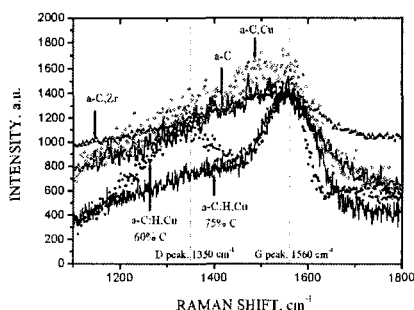


Figure 1. Raman spectra of a-C,(Cu,Zr) and a-C:H,Cu films.

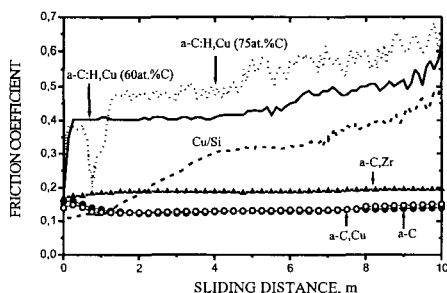


Figure 2. Friction coefficient vs. sliding distance of a-C:H,Cu and a-C,(Cu,Zr) films.

Table 1. Characteristics of RS spectra of a-C,(Cu,Zr) and a-C:H,Cu coatings.

a-C,(Cu,Zr) (CAVD)					
Composition	D-peak, cm ⁻¹	G peak, cm ⁻¹	ΔD , cm ⁻¹	ΔG , cm ⁻¹	I(D)/I(G)
a-C	1393	1556	381	151	2.33
a-C,Cu	1383	1546	308	132	2.52
a-C,Zr	1290	1526	179	216	0.24
a-C:H,Cu (PECVD)					
C at. %	D-peak, cm ⁻¹	G peak, cm ⁻¹	ΔD , cm ⁻¹	ΔG , cm ⁻¹	I(D)/I(G)
25	1337	1551	170	101	1.25
75	1350	1557	280	135	0.71

Spectra from a-C and a-C,(Cu,Zr) films are characterized by the presence of two smeared peaks: ≈ 1340 cm⁻¹ (D peak) and ≈ 1550 cm⁻¹ (G peak). This kind of spectrum with two smeared D and G peaks is characteristic of the so-called “diamond-like carbon” (DLC) films [1,2,6]. The a-C film, obtained by CAVD compared with typical DLC films is characterized by: a) G-peak shift from 1580 cm⁻¹ position for crystalline graphite to lower values; b) I_D/I_G relation is larger than 2.

A comparative analysis of the spectrum parameters obtained from DLC films containing different amount of defects and inhomogeneity with those given in

literature [2,6] leads to a conclusion that a-C film has a high degree of dimensional inhomogeneity of carbon clusters. Cu incorporation into a-C carbon weakly affects the parameters of Raman scattering. The zirconium incorporation influences the characteristics of RS spectra in a special way. G-peak is noticeably shifted from its initial position to lower wave length region, FWHM of G peak increases and the I_d/I_g ratio becomes 0.24. Such RS spectra parameters mean that a large part of carbon clusters in a-C, Zr is fixed by sp^3 bonds [1,2]. Thus, carbon clusters are 3-5 nm. The concentration of ordered graphite clusters is small. This carbon film called a-C [1,2].

It was found that the hardness of a-C and a-C,Cu is approximately equal to 4 and 5 GPa, respectively. The ta-C,Zr films have the maximal hardness of ~ 15 GPa.

The changes of the friction coefficients of a-C and (a-C,Cu) depending on the sliding path are similar (Fig. 2). If the film has a uniform hardness depth distribution and the indenter does not change its form while rubbing, the increase of friction coefficient reflects a gradual increase of the real contact area [7]. If the indenter remains in the film during rubbing, a quicker film wear corresponds to a quicker growth of the real contact area and, accordingly, to quicker increase of the friction coefficient with increasing sliding distance. For (ta-C,Zr) films the friction coefficient does not practically change with increasing the sliding distance although the magnitude of friction coefficient is larger for (ta-C, Zr) films than for a-C and (a-C, Cu) films because of higher film hardness.

The copper grain size and concentration of carbon atoms in the films are dependent of CH_4 concentration in the gaseous phase (Fig. 3). The carbon content increased progressively from 25 to 75 at.% as the CH_4 concentration in the gaseous phase increased from 60 to 100%. Copper grain size became less than 5 nm due to the increase of carbon content in the films from 60 to 75 at.%.

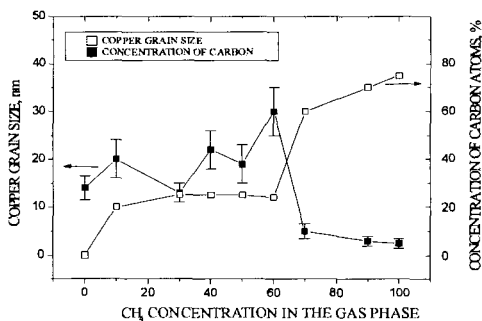


Figure 3. Copper grain size and concentration of carbon atoms vs. concentration of CH_4 in gas phase for a-C:H,Cu coatings deposited by PECVD.

Raman scattering spectra from a-C:H,Cu films with 60 and 75 at.% of carbon are shown in Fig. 1. The decrease of I_d/I_g ratio in comparison with a-C and a-C,Cu films was observed (Table 1). The position of G peak (for 75 at.% C) corresponds to crystalline graphite. Thus, carbon clusters of a graphite predominate in the film

structure. Hardness of a-C:H,Cu films changes in the range of 1.9-2.6 GPa and does not unambiguously depend on the concentration of carbon in the composite film.

Fig. 2 shows the results of a-C:H,Cu film friction tests depending on their composition. One can distinguish three regions. Consider the dependence for Cu film on Si substrate as an example. The region on the graph of the sliding distance from 0 to 4, where the friction coefficient increases nearly linearly with the increase in the sliding distance corresponds to the indenter friction only in the Cu film. A transition region from 4 to 6 corresponds to the indenter friction both in the Cu film and on a very smooth Si surface. In the region above 6 the friction coefficient exhibits a great rise of the magnitude which corresponds to the penetration of a greater part of the indenter into Si.

Thus, the sliding distance characterizes the wear resistance of the film. On the basis of the obtained results one can conclude that the wear resistance of the film decreases with increasing carbon concentration.

4 Conclusions

It is found that (a-C:H,Cu) coatings with C concentration up to 25 at.% have hardness up to 2.6 GPa and good wear resistance. Plasticity of Cu grains and low hardness of a-C:H structure are the reasons of low hardness of (a-C:H,Cu) composite coatings. a-C,(Cu,Zr) coatings (CAVD) have a higher hardness and wear resistance than (a-C:H,Cu) coatings. The change of carbon structure in case of CAVD process takes place by means of assisting ion flux with higher energy than that of PECVD process. During (ta-C,Zr) film deposition one can observe the formation of a-C carbon which has a high concentration of sp^3 fixed nanostructured carbon, that, in its turn provides the highest hardness up to 15 GPa and wear resistance of the composite film.

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ELECTRONIC STRUCTURE OF METALLIC SINGLE-WALL CARBON NANOTUBES: TIGHT-BINDING VERSUS FREE-ELECTRON APPROXIMATION

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For metallic single-wall carbon nanotubes the free-electron model of electronic structure with finite thickness of the conducting shell is proposed. The band structure calculations in the frame of this model of armchair (n, n) nanotubes (for $n = 5-10$) show essential similarity with tight-binding description.

1 Introduction

The tight-binding (TB) approximation is commonly used for theoretical consideration of the electronic structure of carbon nanotubes [1]. But it is desired to have a simpler qualitative model to predict physical properties of nanotubes without bulky numerical calculations and to assist in analysis of experimental data. For example, in [2] the free-electron (FE) model has been used. The aim of this work is to improve this model by taking into account the finite thickness of nanotube conducting layer. We compare our FE approximation with the commonly used TB approach to determine its area of application.

2 Theory

Let us consider a metallic carbon nanotube of the radius r_n as a coaxial conductor, filled with the gas of noninteracting electrons moving on a uniform positive neutralizing background (jelly model). The mean field for moving electrons can be represented as a coaxial well with infinite walls. Thus, electrons cannot leave the well. The width of this well (the radius difference of two cylindrical surfaces) is chosen to be approximately equal to the layer-layer separation 2Δ of graphite.

The motion of an electron is described by the Shrödinger equation (in the cylindrical coordinates):

$$-\frac{\hbar^2}{2m_0} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{m_0}{m_\varphi} \frac{\partial^2}{\partial \varphi^2} + \frac{m_0}{m_z} \frac{\partial^2}{\partial z^2} \right) \Psi + U(\rho) \Psi = E \Psi, \quad (1)$$

where m_φ , m_z — effective masses of an electron (for a given nanotube), moving in the corresponding directions, m_0 — free electron mass. Since the nanotube is

composed of a single atomic layer, there is no need to use radial effective mass. Potential $U(\rho)$ is 0 for $\rho \in [r_n - \Delta; r_n + \Delta]$ and infinite for $\rho \notin [r_n - \Delta; r_n + \Delta]$.

Let us represent the wave function in the form $\Psi = R(\rho) Z(z) \Phi(\varphi)$. Its substitution into (1) gives:

$$\frac{m_z}{m_0} \left(\frac{R''}{R} + \frac{1}{\rho} \frac{R'}{R} \right) + \frac{1}{\rho^2} \frac{m_z}{m_\varphi} \frac{\Phi''}{\Phi} + \frac{Z''}{Z} = - \frac{2 m_z}{\hbar^2} E. \quad (2)$$

Solving this equation for Z , we obtain the eigen-value k — the wave-number corresponding to the plane wave along the tube axis $Z(z) = \exp(ikz)$.

Transforming (2) into

$$\frac{m_\varphi}{m_0} \left(\rho^2 \frac{R''}{R} + \rho \frac{R'}{R} \right) + \frac{\Phi''}{\Phi} = \left(k^2 - \frac{2m_z}{\hbar^2} E \right) \frac{m_\varphi}{m_z} \rho^2 \quad (3)$$

and solving it for Φ we obtain the eigen-value μ , corresponding to the azimuthal standing wave $\Phi(\varphi) = \exp(i\mu\varphi)$. Bessel's equation for the radial wave function follows from (3):

$$R'' + \frac{1}{\rho} R' + \left(\lambda^2 - \frac{m_0}{m_\varphi} \frac{\mu^2}{\rho^2} \right) R = 0, \quad (4)$$

where $\lambda^2 = (2m_0/\hbar^2)E - (m_0/m_z)k^2$.

General solution of (4) is $R = C_1 J_{\xi\mu}(\lambda\rho) + C_2 Y_{\xi\mu}(\lambda\rho)$, where $\xi = \sqrt{m_0/m_\varphi}$; $J_{\xi\mu}(\lambda\rho)$, $Y_{\xi\mu}(\lambda\rho)$ are Bessel functions of the first and the second kind, respectively [3].

The boundary conditions $R(r_n \pm \Delta) = 0$ lead to the secular equation:

$$J_{\xi\mu}[\lambda(r_n - \Delta)] Y_{\xi\mu}[\lambda(r_n + \Delta)] - J_{\xi\mu}[\lambda(r_n + \Delta)] Y_{\xi\mu}[\lambda(r_n - \Delta)] = 0$$

from which we get the sequence of eigen-values $\lambda_v(\xi\mu)$, where v is the number of nodes of the radial wave function

$$R(\rho) = J_{\xi\mu}[\lambda\rho] Y_{\xi\mu}[\lambda(r_n - \Delta)] - J_{\xi\mu}[\lambda(r_n - \Delta)] Y_{\xi\mu}[\lambda\rho].$$

The energy dispersion is specified by relation

$$E_{v,\mu}(k) = \frac{\hbar^2}{2m_z} k^2 + \frac{\hbar^2}{2m_0} \lambda_v^2(\xi\mu). \quad (5)$$

This means that the full energy is the sum of the kinetic energy of a longitudinal motion $E_{\parallel}(k) = (\hbar^2/2m_z) k^2$ and transversal motion energy $E_{\perp}(v,\mu) = (\hbar^2/2m_0) \lambda_v^2(\xi\mu)$. In comparison with the infinitely thin wall model [2] we have an additional radial quantum number v . This leads to the appearance of nondegenerate transversal energy levels corresponding to $\mu = 0$ (shown in Fig. 1a by dashed lines), in opposite to [2], where all energy levels (except ground) are doubly degenerate.

The valence electron density ρ_e in the tube wall is specified by the relation

$$\rho_e = \frac{N}{2\pi r_n \Delta L}, \quad (6)$$

where N is the number of atoms in the unit cell of the length L . One can evaluate the number of electrons in the unit cell via Fermi wave vector $k_F(v,\mu)$, i.e.

$$N = 4 \sum_{\nu, \mu} \gamma_{\nu, \mu} \frac{L}{2\pi} k_F(\nu, \mu), \quad (7)$$

where the summation is taken over all filled subbands and $\gamma_{\nu, \mu}$ is the degeneracy factor of a given subband ($\gamma_{\nu, \mu} = 1$ for $\mu = 0$ and 2 otherwise). The factor 4 in (7) is due to two spin projections and two signs of wave number $\pm k$.

Taking into account (5) – (7) we obtain

$$\rho_e = \frac{1}{4\pi^2 r \Delta} \sqrt{\frac{m_z}{m_0}} \sum_{\nu, \mu} \gamma_{\nu, \mu} \sqrt{E_F \frac{2m_0}{\hbar^2} - \lambda_v^2(\xi, \mu)}.$$

Solving this equation for the number of filled zones and E_F one can determine the Fermi energy.

3 Calculations for armchair nanotubes

Our model operates with four parameters: 1) longitudinal effective mass m_z ; 2) azimuthal effective mass m_ϕ ; 3) thickness of a conductive layer 2Δ ; 4) effective nanotube radius r_n . The agreement with experiments or with existing approximations can be obtained by a variation of these parameters.

Let us fix the parameter $2\Delta = 0.34$ nm which is equal to the graphite inter-layer separation. The chirality and the radius of single-wall carbon nanotube are uniquely specified by the chiral vector $\mathbf{C}_h = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \equiv (n_1, n_2)$, where n_1, n_2 are integers and $\mathbf{a}_1, \mathbf{a}_2$ are the unit cell basis vectors of graphite [1]. The chiral vector $\mathbf{C}_h$ is a circumferential lattice vector defined on nanotube surface, and $\mathbf{C}_h$ is perpendicular to the tube axis. For armchair nanotubes $n_1 = n_2 = n$, and the tube radius r_n is defined by $r_n = |\mathbf{C}_h|/2\pi \equiv a\sqrt{3}n/2\pi$, where $a = 0.249$ nm is the lattice constant for graphite. These values of r_n are used in our calculations.

Until now there are no experiments with specific single-wall carbon nanotubes to evaluate the effective masses of charge carriers. So we compare the band structure obtained in the TB approximation with that obtained in our model.

In the TB approximation with only the nearest neighbors taken into account the dispersion relation for the energy of an electron in carbon nanotube is [4]

$$E(j, k) = \pm \gamma_0 \sqrt{3 + 2 \cos(ak) \pm 4 \cos(ak/2) \cos(j\pi/n)},$$

where $j = 0, \dots, n-1$ and k changes in the range of Brillouin zone boundaries of the nanotube ($-\pi/a; \pi/a$); γ_0 is nearest-neighbor transfer integral.

We have carried out calculations for armchair nanotubes in the range of indices $n = 5-10$. The longitudinal effective mass m_z was taken to be equal to the TB effective mass $m_z \approx m_0$. The azimuthal effective mass m_ϕ was chosen to adjust the Fermi level E_F in our model to the TB value. We use $\gamma_0 = 2.7$ eV from [5], which gives $E_F = 8.1$ eV. For these conditions $m_\phi \approx 1.3m_0$ for all nanotubes considered.

The results of the calculations for (5, 5) nanotube are presented in Fig. 1. One can see the similarity of TB and FE band structures in the vicinity of the zone

center. The number of filled subbands also coincides in both models. The radial distribution of the valence electron density is shown in Fig. 1b. The maximum of the density is slightly shifted outside the tube due to high values of μ quantum numbers.

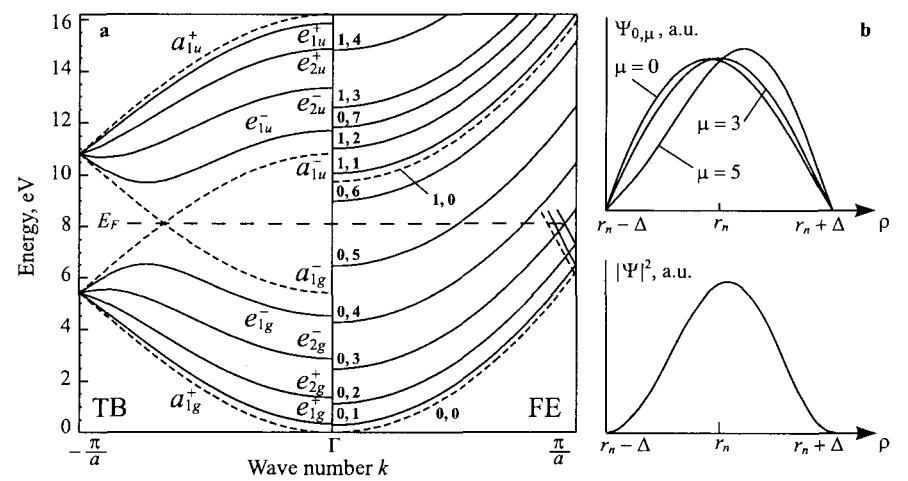


Figure 1. a. Band structure of armchair (5,5) nanotube in TB (from [4]) and FE approximations. Solid lines denote twofold degenerate subbands, dashed lines — nondegenerate. Indices v, μ are written above the corresponding band. $\gamma_0 = 2.7$ eV, $E_F = 8.1$ eV, $m_z = 0.98 m_0$, $m_\varphi = 1.27 m_0$. **b.** Wave functions $\Psi_{0, \mu}$ and valence electron density $|\Psi|^2 = \sum_{\mu=0}^5 \gamma_{0, \mu} |\Psi_{0, \mu}|^2$, the subband with $v = 0, \mu = 5$ is half-filled.

In conclusion, we have shown the essential similarity of TB and FE descriptions of armchair carbon nanotubes. The proposed model can be easily improved to include the electron-electron exchange and correlation effects.

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CONDUCTIVITY OF METAL – LINEAR CARBON CHAINS WITH METAL INCLUSIONS – METAL STRUCTURES

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Carbon chain structures with an inclusion of metals are studied. Lengths of the carbon chains in many orders exceed their diameter. I-V characteristics of metal – linear carbon chains with metal inclusions and the basic parameters have been determined. The dependence of I vs U for the structures is described by the linear law ($U < 0.3$ V) and the U^3 law ($U > 0.3$ V). The type of the conductivity depends on the step of thermal cycle (heating or cooling).

1 Introduction

The molecular structure of linear carbon (carbine) is the chain with sp -hybridized atoms [1]. In order to explain a variety of carbene forms the structure of carbon chains with possible two types of bonds (Fig. 1) in the zigzag model was offered: with polyene solid state $[-(C \equiv C)-]_n$ and cumulene $[=(C=)]_n$ fragments. For a polymeric carbon chain in solid state the zigzag structure with cumulene type of connection is most probable. It can be packing of zigzag carbon chains with linear sites of different length.

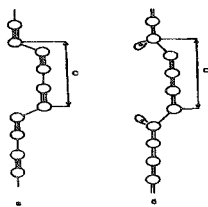


Figure 1. Model of zigzag carbon circuits construction.

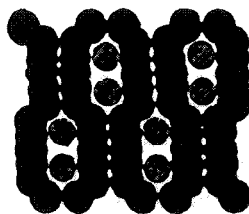


Figure 2. Model of a carbene structure.

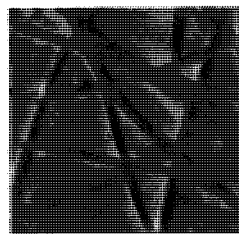


Figure 3. The optical image of carbene microstring.

On the basis of experimental measurements and theory it is possible to assume that formation of carbene results in association of short carbon chains with simultaneous packing of a small amount of metals in empty places of the carbon matrix (Fig. 2). Together with the basic part, which consists of carbon atoms, the

carbine also can contain atoms of metals. That was experimentally confirmed using the research of elemental composition by the laser mass-spectroscopy. The inclusion of Mg, Al, Ti, Fe, Zn was detected.

The method of IR-spectroscopy for studying linear carbon carbine was used. The presence of C=C and C-C bonds gives the basis to assume, that the carbon sample under study such as carbine consists of polymeric circuits of carbon with cumulene type of connection. The existence of C-C bonds confirms the zigzag model of carbon circuits.

2 Experiment

Samples of carbon structures with the linear chains as carbine (Fig. 3), which were made in Institute of Adsorbents of National Academy of Sciences of Ukraine are studied. The separate carbine strings with length of 0.5-1 cm, an interlacing of strings (garrot) and garrot of strings in the pressed kind were used.

A laser-scanning profilometer (differential microscope -LSP) was utilized for optical imaging.

Tunnel current-voltage characteristics (I-V) of (Pt/Ir edge)/microstring, (Pt/Ir edge)/(garrot of microstrings) or structure Sn (Cu)/microstring (the current proceeds along a surface carbine composite or a microstring) were measured. Measurements made with the equipment similar to scanning tunneling spectroscopy constructed in Laboratory of Radiophysical department. Accuracy of the current measurement was 0.01 nA. The time of the record at the change of voltage from 0 to +3 V (or -3 V) with the step of 25 mV was 30 s, the temperature interval was $20 < T < 325$ K.

3 Results and discussion

1. I-V characteristics of pressed garrot of carbine microstrings were measured at 300 K at the change of voltage in the range of ± 0.3 V. The current through the sample was ± 60 μ A. The linear I-V characteristics were observed. The resistance of pressed garrot of carbine microstrings was 6.38 k Ω and resistivity was 22.5 Ω ·m.

2. I-V characteristics were measured at temperatures $300 < T < 325$ K. The voltage changed in the range of ± 3 V; the current through the sample was ± 100 μ A. It was observed asymmetric behaviors of I-V characteristics with hysteresis (Fig. 4). The resistance of garrot of carbine microstrings was $13 < R < 40$ k Ω and resistivity was $52 < \rho < 160$ Ω ·m.

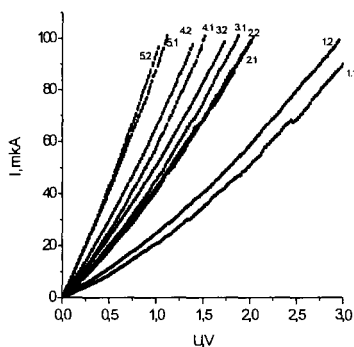


Figure 4. I-V characteristics of pressed garrot of carbine microstrings at different temperatures: 1- 300 K, 2 - 305 K, 3 - 310 K, 4-315 K, 5-320 K.

3. I-V characteristics of garrot of carbine microstrings were measured at 300 K at change of the voltage in the range of ± 0.8 V. The current through the sample was $\pm 10 \mu\text{A}$. It was observed asymmetric behaviors of I-V characteristics with hysteresis. The resistance of garrot of carbine microstrings was $60 \text{ k}\Omega$ and resistivity was 27Ω

4. I-V Characteristics of individual carbine strings were measured at temperatures $20 < T < 300 \text{ K}$. The voltage changed in the range of $\pm 2 \text{ V}$, the current through the sample was 0.5 mA . The linear behavior of I-V characteristics was observed at the current up to 0.1 mA and asymmetric behavior at the greater current. Hysteresis is also presented. The constructed dependence of the normalized conductivity $(U/I) \cdot dI/dU$ versus U is shown in Fig. 5. The energy band gap is near 2.5 eV .

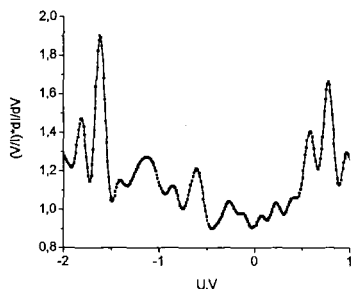


Figure 5. Dependence of the normalized conductivity $(U/I) \cdot dI/dU$ versus U for pressed garrot of carbine microstrings.

The energy of activation of the charge carriers was 0.4 eV . The resistance of carbine microstrings was $4 \text{ k}\Omega$ and resistivity was $0.025 \Omega \cdot \text{m}$. I-V characteristics of microstrings 1 and 2 have different character depending on a thermal cycle. The microstring 1 at the cooling and heating steps has the metal type of conductivity whereas microstring 2 at the heating step shows the semiconductor type of conductivity (Fig. 6).

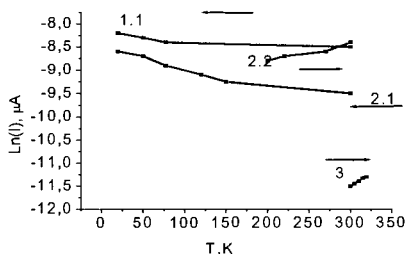


Figure 6. Conductivity versus temperature for: 1.1 – individual microstring 1 (cooling), 2.1– individual microstring 2 (cooling), 2.2 – individual microstring 2 (heating), 3 - pressed garrot of carbine microstrings (heating).

Comparing the results for individual carbine microstrings and carbine composite, we can see that the resistivity of the carbine composite exceeds considerably that for the individual microstring, whose resistivity in turn is close to the corresponding magnitude for graphite.

4 Conclusion

The resistivity of carbine composite is determined by points of the contact between adjacent strings rather than by the features of individual microstrings. The different type of the conductivity of the sample on different thermal cycles is observed. It is possible to be explained by a non-uniform structure of carbine which contains impurity of metals and plays the role in conductivity of microstrings.

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INFLUENCE OF Si(111)-[($\sqrt{3}\times\sqrt{3}$)/30°]-Cr SURFACE PHASE ON GROWTH AND CONDUCTIVITY OF DISORDERED IRON 2D LAYERS ON Si(111)

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Conductivity through disordered iron layers during its formation on Si(111)-7x7 and Si(111)-[($\sqrt{3}\times\sqrt{3}$)/30°]-Cr surface phase was investigated. Silicide formation on Si(111)7x7 surface is observed, but Si(111)-[($\sqrt{3}\times\sqrt{3}$)/30°]-Cr surface phase behaves like a diffusion barrier for iron atoms. Nucleation and growth of iron islands proceeds with increasing of metal thickness without formation of iron silicide. Iron forms continuous two dimensional metal layer with near bulk parameters starting from the thickness of 1 nm.

1 Introduction

It is known that iron atoms diffuse in atomically clean silicon substrate [1] during submonolayer deposition in ultrahigh vacuum conditions. Such behaviour complicates the growth of two-dimensional iron layers for obtaining ferromagnetic properties. The ordered surface phases could influence the growth mechanism and morphology of two-dimensional iron layers on silicon. Conductivity and Hall measurements could give additional information about the growth and conductivity mechanisms in similar systems.

In this paper we compare conductivity of p-type silicon substrates with initially formed Si(111)-7x7 and Si(111)-[($\sqrt{3}\times\sqrt{3}$)/30°]-Cr surface phase during submonolayer and monolayer deposition of iron at room temperature.

2 Experimental details

The film growth and electrical measurements were performed in the ultra high vacuum (UHV) chamber with a base pressure of $1\cdot 10^{-9}$ Torr. It was equipped with LEED optics, evaporation unit with three sublimation sources (Si, Cr, Fe) and manipulator with samples holder and a quartz thickness sensor. In situ electrical measurements were conducted using automated UHV Hall installation [2]. The p-type ($10\ \Omega\cdot\text{cm}$) Si(111) wafers were used as substrates. The native oxide and

residual carbon contaminants were removed in the chamber by direct current annealing at $700\div 800^{\circ}\text{C}$ for 20-30 min and finally by flashing at 1200°C . The silicon surface was controlled by LEED. Metal (Fe, Cr) deposition rates were about $0.001\div 0.002$ nm/s. Si(111)- $[(\sqrt{3}\times\sqrt{3})/30^{\circ}]$ -Cr surface phase was formed by 350°C annealing of 0.3 nm Cr layer deposited onto Si(111)7x7 surface. Disordered iron films were grown using layer by layer adsorption at room temperature. Registration of Hall and longitudinal voltage was made on each growth step.

3 Results and discussion

There were two kind of experiments on Si(111)7x7. The first was conducted on the atomically clean silicon surface right after loading of the sample and its high temperature annealing. The sample showed bright Si(111)-(7x7) LEED pattern. The Hall voltage (U_H) and longitudinal voltage (U_p) versus iron thickness are presented in Fig. 1. Within the range of $0\div 0.15$ nm main changes occur with U_p (Fig. 1b), but U_H shows weak decreasing (Fig. 1a). At $d_{\text{Fe}}\approx 0.12$ nm U_p has maximum. It corresponds to rising of the resistance on 6% compared with initial conditions. Increasing of the resistance during a dsorption of metal submonolayer was earlier registered for silver [3], lead [4] and gold on Si(111)7x7 [3]. We justify this effect on the basis of appearance and recharging of some additional surface states, formed by iron atoms. They diffuse under the silicon surface at the very beginning of deposition [1], and give rise to the deep donor states. Electrons from this states partially compensate huge hole amount in p-type substrates which results in decreasing of conductivity. Some excess numbers of silicon atoms [1] go out from silicon lattice on the surface and form the silicide clusters with deposited iron atoms. Nucleation of iron silicide islands takes place at $0.05\div 0.1$ nm. Coalescence of this islands and formation of percolation paths begins at $0.1\div 0.3$ nm of Fe. This

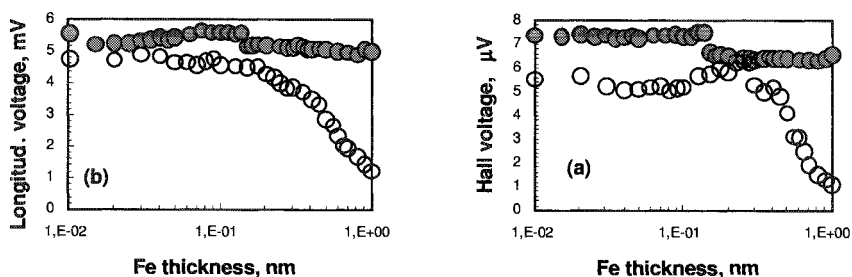


Figure 1. Hall voltage (a) and longitudinal voltage (b) versus iron thickness. Deposition on Si(111)7x7 – filled circles; on Si(111)- $[(\sqrt{3}\times\sqrt{3})/30^{\circ}]$ -Cr – open circles.

fact is confirmed by the abrupt decrease both the Hall and longitudinal voltages (Fig. 1). Further decreasing of these parameters corresponds to the formation of

percolation paths between iron enriched silicide islands. Calculations in the frame of two-layer model [5] give the following characteristics of this system at $d_{Fe} \approx 0.8$ nm: majority carriers – holes; bulk concentration – $4 \cdot 10^{19} \text{ cm}^{-3}$, mobility – $175 \text{ cm}^2/\text{V}\cdot\text{s}$. So, the formed iron silicide layer on p-type silicon displays the properties of generated semiconductor. The Fe-Fe metallic bonds are formed at higher Fe coverages (more than 2 nm).

The second part of our work concerned layer by layer iron growth on previously formed $\text{Si}(111)-[(\sqrt{3} \times \sqrt{3})/30^\circ]\text{-Cr}$ surface phase. The Hall and longitudinal voltage versus iron coverage are also shown in Fig. 1. Both curves sharply decrease from the beginning and fall almost to zero at 1.0 nm. A small decrease of the Hall voltage in the range 0–0.03 nm can be connected apparently with doping of $\text{Si}(111)-[(\sqrt{3} \times \sqrt{3})/30^\circ]\text{-Cr}$ surface phase by iron. On the second growth stage (0.03–0.1 nm) nucleation of iron islands takes place, and there is no changes in conductivity. The Schottky barrier is formed between Fe islands and surface phase in the range of 0.1–0.2 nm. It results in changes of conductivity

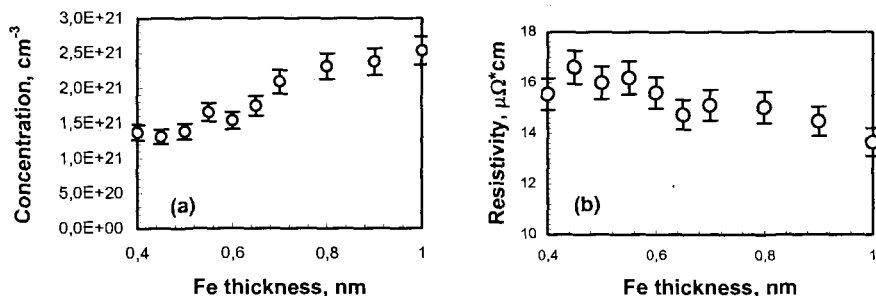


Figure 2. Bulk concentration (a) and bulk resistivity (b) of iron 2D layer versus iron thickness. Iron is deposited on $\text{Si}(111)-(\sqrt{3} \times \sqrt{3})/30^\circ\text{-Cr}$ surface phase.

mechanisms in the silicon substrate and an increase of the Hall voltage. Formation of percolation channels and two-dimensional continuous film takes place at 0.2–0.87 nm (Hall and longitudinal voltage rapidly decrease). As a result, Fe atoms form a continuous two dimensional metal layer at 1 nm or at near 12 monolayers of iron (one iron monolayer has the thickness 0.083 nm). Such kind of behavior proves that $\text{Si}(111)-[(\sqrt{3} \times \sqrt{3})/30^\circ]\text{-Cr}$ surface phase is a diffusion barrier for iron atoms, which prevents intermixing of Fe and Si atoms. One-layer model calculations showed, that conductivity in this film supported by holes (majority carriers) with following parameters: bulk concentration – $2.5 \cdot 10^{21} \text{ cm}^{-3}$ (Fig. 2a), hole mobility – $180 \text{ cm}^2/\text{V}\cdot\text{s}$ and bulk resistivity – $13.6 \mu\Omega\cdot\text{cm}$ (bulk resistivity of iron is $8.7 \mu\Omega\cdot\text{cm}$).

4 Conclusions

Conductivity through disordered iron layers during its formation on Si(111)-7x7 and Si(111)-($\sqrt{3}\times\sqrt{3}$)/30°-Cr surface phase has been investigated. It was established that at submonolayer iron coverings on Si(111)-7x7 iron atoms diffuse under the silicon surface which results in the formation of silicide islands. The layer conductivity given by coalescence of iron silicide islands was observed at 0.8-1.0 nm of iron coverage with bulk concentration of $4\cdot 10^{19} \text{ cm}^{-3}$ and hole mobility of $175 \text{ cm}^2/\text{V}\cdot\text{s}$. Iron deposition at small coverages on Si(111)-[($\sqrt{3}\times\sqrt{3}$)/30°]-Cr results in doping of this surface phase with Fe atoms and then in formation of the diffusion barrier for iron atoms. Nucleation and growth of iron islands proceed with the increase of metal thickness without formation of silicide. Metal conductivity through the continuous iron layer begins at 1.0 nm with bulk concentration of $2.5\cdot 10^{21} \text{ cm}^{-3}$, hole mobility of $180 \text{ cm}^2/\text{V}\cdot\text{s}$ and bulk resistivity $13.6 \mu\Omega\cdot\text{cm}$.

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MODELLING VERTICAL TUNNELING IN SEMICONDUCTOR MULTIPLE QUANTUM WELL STRUCTURES: EFFECT OF THE DISORDER IN LAYER PARAMETERS

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We model the vertical electron transport in semiconductor multiple quantum well structures at low temperatures. A disorder is introduced into the layer parameters, namely, widths or potentials of the quantum wells or barriers. Field-dependent electron transmission spectra and current-voltage characteristics are calculated for various types and degrees of the disorder.

1 Introduction

Since the paper by Esaki and Tsu [1], many efforts in superlattice growth were made to obtain a perfect periodic structure. On the contrary, the random superlattices were proposed in [2]. Semiconductor multiple quantum well (MQW) structures with an intentional disorder were grown and investigated in [3,4]. The disorder was introduced there by a regulated randomization of the well width values. Such structures exhibit a number of interesting optical and electrical properties. This type of the disorder strongly influences the electron transport along the growth direction (vertical transport) [5]. The transport theory in perfect periodic structures is well-developed (see e.g. [6] and references therein). However, it cannot be applied for the disordered systems because of the absence of the translational symmetry. Interlayer hopping probabilities were studied in [7]. In the current work we study theoretically vertical tunneling transport in the disordered MQW structures.

2 Model

We consider semiconductor MQW structures with mono-polar conductivity and low carrier concentration, at low temperatures. Resonant tunneling approach to the vertical transport is adopted which is applicable when the carrier tunneling time is less than the carrier free time: $\tau_{\text{tunn}} \ll \tau_{\text{scatt}}$.

The resonant tunneling time can be estimated as $\tau_{\text{res}} \approx m\kappa^2 d^4 \exp(N\kappa b) / (2\pi^3 \hbar)$, where $\kappa^2 \approx 2mU/\hbar$, U is the barrier height, d and b are the well and barrier widths, respectively, and N is the number of barriers. Scattering by optical and acoustical

phonons and the Coulomb scattering processes are usually most important. Their rates can be estimated in a straightforward way using ordinary bulk formulae [8]. To avoid intensive PO-scattering, we consider a limited bias interval $eV < eV_{max} \approx \hbar\omega_{PO}$, and below only these values will be considered. To extend the voltage interval, we choose the structure material having the greatest PO-phonon energy, which is GaN. Taking its parameters, we find that for $N=6$ quantum barriers, each 3 monolayer wide and 100 meV high, and 5 wells, each 12 monolayer wide, the characteristic times are following: $\tau_{res} \approx 2 \cdot 10^{-11}$ s, $\tau_{DA} \approx 1 \cdot 10^{-10}$ s, $\tau_{Coul} \approx 5 \cdot 10^{-10}$ s.

We use the effective mass approximation. The structure potential is approximated by a consequence of rectangular quantum barriers and wells. Their widths and potentials are randomly varied with the uniform distribution. The sequence of the parameters is calculated by a random number generator. Other parameters, e.g. effective masses of the carriers, are assumed equal in different layers. To simplify the transmission coefficient calculations, we approximate the electric field potential by a step function. The transmission coefficient is calculated using the transfer matrix method [9]. The I - V curves of the MQW structures along the x -axis (growth direction) are derived from the calculated transmission spectra [10].

3 Results and discussion

The calculated electron transmission spectra for various degrees of disorder σ in the

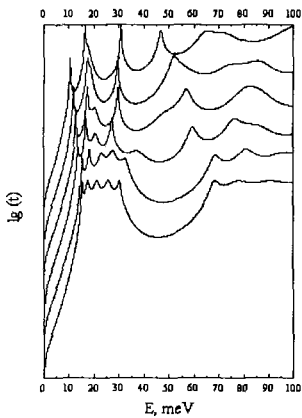


Figure 1. Zero-field electron transmission spectra of the disordered MQW structures with well width fluctuations: periodic structure (bottom), $\sigma = 17\%$, $\sigma = 33\%$, ..., $\sigma = 83\%$ (top).

well widths are shown in Fig. 1. This type of disorder influences the transmission coefficient significantly. The peaks of the spectrum correspond to resonant tunneling via an electron energy level within the MQW structure, and these levels form a quasi-subband. In an electric field the Bloch electron states become quasi-localized, and qualitatively we can treat each of them as localized in its own quantum well. They shift to lower energies as the voltage increases, with the well bottom. The energy subbands widen and finally overlap. Effect of the disorder can be, in some sense, compared with that of the electric field; the size quantization energy in each quantum well depends strongly on the well width. As a result, energy level intersections become possible within the same subband when an

electric field is applied. The disorder in the barrier widths also affects the transmission spectra, but, as compared with the spectra of the structures containing disorder in well widths of the same degrees, the spectra for fluctuating barrier widths do not differ much from that of a periodic system.

A sample I - V curve of a disordered MQW structure with relatively small well width fluctuations is depicted in Fig. 2. Similarly to one of the periodic structure, it

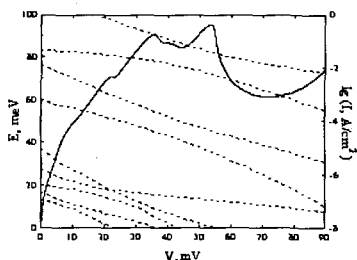


Figure 2. Current-voltage characteristic (solid curve) and transmission maxima energies vs. voltage (dashed curves) for the disordered structure with well width fluctuations, $\sigma = 33\%$.

exhibits few current drops originating from the "disappearance" of the electron states, when they move below the conduction band bottom in the cathode so that the transport through such state is no longer possible. The exact positions of the current drops depend on the particular realization of the disorder. In addition, one should notice a curve bend at low voltage following the Ohmic interval of the I - V characteristic. This curve bend corresponds to the (anti)crossing of the levels at relatively low energy, absent in the periodic system. Obviously, fluctuations of the compositions of wells or barriers, i.e. fluctuations of their

potentials, also lead to the changes in the structure characteristics. Mixed types of the disorder can be studied. The subband structure, and thus, the transport properties of the MQW structures can be controlled by intentional disorder.

Acknowledgements

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ELECTRONIC PROPERTIES OF NANOCRYSTALLINE CHROMIUM DISILICIDE

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Simple approach based on the effective mass theory has been developed and successfully applied to simulate electronic properties of monocrystalline and grained nanocrystalline films accounting for the confinement effect and interactions between the grains. Quantum confinement was found to influence band gap values only for the films with the thickness less than 5 nm. The highest gap varied from 0.63 to 0.91 eV depending on the film thickness as well as on the lateral size of the grains. Inclusion of the grains inside the film induces a considerable increase of the gap as compared to the monocrystalline film of the same effective thickness.

1 Introduction

Semiconducting silicides epitaxially grown on silicon have gained an increased practical interest to be used in novel semiconducting devices due to their high thermal stability, homogeneous interface and smooth surface morphology [1]. Low-dimensional structures are the main object of study and application in nanoelectronics. When the structure size in one direction decreases up to several nm, its properties may differ essentially from the bulk properties of a source material. Such modification of the properties looks attractive.

The most well investigated chromium disilicide is one of the possible candidates for the formation of nanofilms. This material has the minimal mismatch with a silicon substrate (less than 0.2% for $\text{CrSi}_2(0001)/\text{Si}(111)$ orientation) in comparison with other transition metal silicides as was confirmed by the epitaxial results [2-4]. Different types of the films were formed: high quality epitaxial as well as nanocrystalline consisting of single grains. That allows to work with various types of nanoobjects. One of the favorable fields of application of semiconducting silicides is thermoelectric energy conversion devices and sensors. Recent studies show that thermoelectric efficiency of the compound can be greatly increased while using low-dimensional (especially multi-layer) structures as compared to the bulk material [5]. We have developed a simple analytical approach based on the effective mass theory (EMT) that can be effectively applied to the electronic property simulation of complicated silicide nanostructures. The approach has been recently successfully applied to silicon nanostructures [6].

2 Application of the EMT to estimate the energy gap

The dependence of the energy gap on the film thickness can be explained within the EMT. If one assumes the free carrier motion is confined in (111) direction and the confinement affects both electrons and holes, the following formula can be applied for the gap (E_g) evaluation of the system

$$E_g = E_{go} + \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \cdot \frac{\pi^2 \hbar^2}{2d^n}, \quad (1)$$

where E_{go} is the band gap of the bulk material, d is the film thickness, m_e^* and m_h^* are the effective masses of bulk material in the confinement direction of electrons and holes, respectively. For ideal infinite rectangular well the exponential power $n=2$. Usually for real structures n is smaller than 2 because the shape of the potential barrier in the near surface region may differ from the simple step-like function, that was observed for various silicon nanostructures [7].

The equation (1) is used for ideal 2D monocrystalline films. However, real structures usually contain separate grains with preferable orientations respect to the substrate. These may drastically change the properties of investigated structures in comparison with idealized models. That explains the difference in calculated and measured properties of silicon nanostructures [6]. The band gaps for the grained films are located somewhat higher on the energy scale compared to monocrystalline ones. In these cases we have 2D set of interacting quantum boxes that are associated with silicon grains. The intergrain regions may be treated as potential barriers of some height. Therefore, within the EMT the gap increasing in such films can be expressed as an additional term (ΔE_g) which shall be added to (1), so that

$$\Delta E_g = \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \cdot \frac{\hbar^2 \mathbf{K}^2}{2}, \quad (2)$$

where m_e^* and m_h^* are the electron and hole effective masses in the film plane, respectively. The value of $\mathbf{K}^2 = K_x^2 + K_y^2$ can be obtained directly by solving 2D Schrödinger equation with the appropriate Bloch's boundary conditions. For the general case an analytical solution is not possible and one needs to solve the equation numerically. But we found that, for our purposes, one can get qualitatively the same results if the grained films considered, which have the hexagonal symmetry, are represented by an effective 2D set of interacting square wells with rectangular barriers. Thus, to estimate the values of K_x^2 and K_y^2 , for the square lattice inside the unit cell one has two independent Kronig-Penney equations for both electron and hole subsystems.

The time-independent Schrödinger equation for a 2D set of quantum wells is

$$\nabla^2 \Psi + 2m/\hbar^2 (E - U(\mathbf{r}))\Psi = 0, \quad (3)$$

where $U(\mathbf{r}) = \sum V(\mathbf{r} + \mathbf{R})$, $\mathbf{R}$ is the translation superlattice vector, $V(\mathbf{r})$ is the potential of a single well, m is the carrier effective mass, E is the energy. Assuming $V(\mathbf{r})=0$ inside the well, within the unit cell one has

$$\begin{aligned}\nabla \Psi + \mathbf{K}^2 \Psi &= 0 \quad \text{inside the well} \\ \nabla \Psi + \chi^2 \Psi &= 0 \quad \text{outside the well}\end{aligned}, \quad (4)$$

where the momentum $\mathbf{K}^2 = 2mE/\hbar^2$ and $\chi^2 = 2m(V(\mathbf{r})-E)/\hbar^2$. Appropriate Bloch's boundary conditions are

$$\Psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\mathbf{R}}\Psi(\mathbf{r}), \quad (5)$$

where $\mathbf{k}$ is the quasimomentum vector.

For the square well, taking into account that a variable separation is possible for a potential of the form $V(\mathbf{r}) = V_o(\Theta(x) + \Theta(y))$, where Θ is the step-like function which is equal to 0 and 1 inside and outside the well respectively, one has two independent 1D set of equations. Moreover, assuming that $\Psi(\mathbf{r}) = \Psi(x)\Psi(y)$, the Bloch's boundary conditions can be split into two ones for $\Psi(x)$ and $\Psi(y)$ as well. Finally, one has two independent 1D Kronig-Penney problems for K_x and K_y . Thus, for x -direction:

$$\begin{aligned}\cosh(\chi_x b) \cos(K_x a) + \sinh(\chi_x b) \sin(K_x a) \times \\ (\chi_x^2 - K_x^2) / (2K_x \chi_x) = \cos(k_x c)\end{aligned}, \quad (6)$$

where $\chi_x^2 = 2mV_o/\hbar^2 - K_x^2$. The parameters a and b are the lateral size of the well and the barrier, respectively and $c = a + b$. The quasimomentum projection k_x varies in between $\pm\pi/c$. So, it is easy to obtain K_x^2 at the appropriate band edge. Therefore, for the square well one got two identical solutions, i.e. K_x and K_y are the same. This corresponds to the lattice symmetry with respect to $\pi/2$ rotations.

3 Electronic properties of CrSi₂ nanostructures

3.1 Monocrystalline films

The estimation of the energy gap of the CrSi₂ film within the EMT was performed using the computed effective masses of the charge carriers for the bulk chromium disilicide [8] (in units of the free electron mass m_0): for electrons – $m_{xx} = 0.69m_0$; $m_{yy} = 0.66m_0$; $m_{zz} = 1.49m_0$, for holes – $m_{xx} = 1.10m_0$; $m_{yy} = 1.20m_0$; $m_{zz} = 0.82m_0$. The energy gap of bulk material was chosen to be 0.35 eV. The value of n in Eq. (1) was assumed to be 1.93.

The calculated dependence of the band gap (E_g) on the film thickness (d) is shown in Fig. 1(a) along with the maximum possible value within the EMT ($n = 2$).

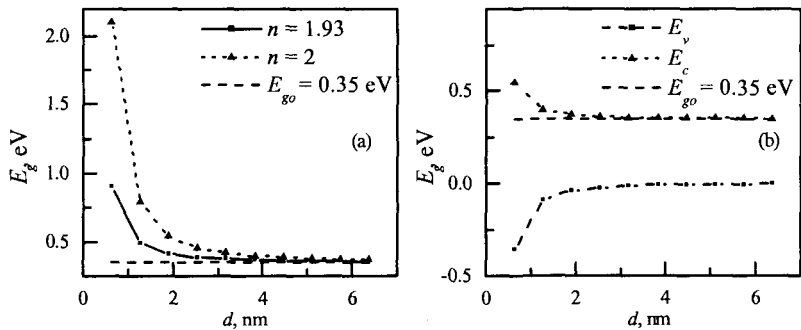


Figure 1. Total band gap (a) and the valence band maximum and conduction band minimum (b) versus monocrystalline film thickness. Dotted lines reproduce the appropriate bulk values.

It is evident that the quantum confinement plays a role mainly in the films thinner than 3 nm. Starting from 5 nm the energy gap of the bulk material is reproduced. The top of the valence (E_v) and the bottom of the conduction (E_c) band energy dependence on the effective film thickness are shown in Fig. 1(b). The most change in the band gap (up to 70% for the film thickness less than 1.5 nm) is due to the confinement of the valence band.

3.2 Nanocrystalline films

The following model parameters were used: the grain size to be $a = 1.3293$ nm, $b = 0.2$ nm, the barrier height V_o to be 0.5 eV. The quantum confinement affecting the carriers inside the grains within the film plane is characterized by the average effective mass $(m_{cx}m_{yy})^{0.5}$ and it is equal to $0.671m_0$ for electrons and to $1.148m_0$ for holes. The results of calculations are presented in Fig. 2.

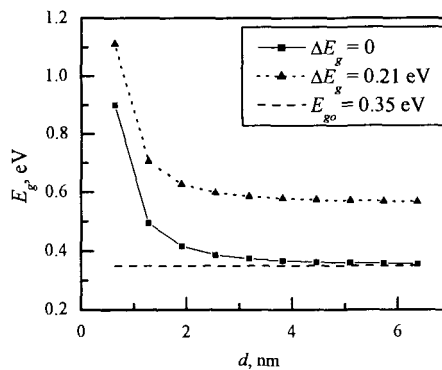


Figure 2. Band gap versus film thickness for monocrystalline ($\Delta E_g = 0$) and grained nanocrystalline ($\Delta E_g = 0.21$ eV) CrSi_2 films.

Energy gap broadening of 0.21 eV or 0.11 and 0.10 eV for the conduction and the valence bands, respectively, takes place. The curves corresponding to the films with larger grains approximately follow the behaviour of E_g versus d for the monocrystalline film with a certain upshift in each case. This upshift can be ascribed to the additional confinement conditions within the plane of the film. Moreover, for the films thicker than 5 nm E_g tends to 0.56 eV that corresponds to experimentally measured value for amorphous CrSi₂ films [9].

4 Conclusion

The electronic properties of monocrystalline and grained nanocrystalline CrSi₂ films were estimated within the Effective Mass Theory. Inclusion of the grains inside the film increases the energy gap up to 60% compared to the monocrystalline film of the same effective thickness.

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CONDUCTIVITY OSCILLATIONS DURING FORMATION OF DISORDERED 2D Yb LAYERS ON Si(111)

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Five stages were resolved during interface formation in Yb/Si(111) system by AES, EELS data and *in situ* Hall measurements. Some amplitude oscillations have been observed in sheet conductivity, hole mobility and surface hole concentration within the Yb coverage range below 6 ML. The conductivity oscillations are explained by transition from semiconductor-type conductivity at the first two-dimensional Yb growth stages to metal-like conductivity of 2D and 3D Yb silicide films.

1 Introduction

Ytterbium silicides, among other rare-earth metal silicides, are promising materials for microelectronics. They have small Schottky-barrier height on the n-type Si surface [1] and are transparent for light [2]. Despite these attractive features of the Yb/Si system, no investigations of technology-oriented electrophysical properties of these materials are known to us so far. In this respect studying of the growth mode and investigation of electrical properties of the Yb/Si system are of great interest.

We studied room temperature film growth modes and electric properties of Yb/Si(111) system by AES, EELS and *in situ* 6-probe Hall measurements. Surface morphology of the films was characterized by atomic force microscopy (AFM).

2 Experimental details

Two series of growth experiments were carried out: 1) AES-EELS investigation of Yb/Si(111) film growth process and 2) *in situ* Hall measurements [4] at room temperature for the Yb/Si(111) system during its formation. P-type ($10 \Omega\cdot\text{cm}$) Si(111) wafers were used as substrates. A thoroughly degassed Ta-cell heated by direct current was used to evaporate Ytterbium (99.99%) onto the Si(111)7x7 surface at room temperature in the UHV chamber. The deposition rate was calibrated with a quartz sensor before the experiments and checked again after that. In both our experiments new portions of Yb were added onto the same sample

surface that was analyzed before. The wide range of coverage, from 0.05 up to 18 ML was studied. Hall and conductivity measurements were carried out *in situ* after Yb deposition onto the Si (111) surface at room temperature. Film morphology was studied by atomic force microscopy (Solver P47 [3]) after unloading of samples from the growth chamber.

3 Results and discussion

Intensity ratios of AES and EELS peaks of the Yb/Si(111) system are summarized in the Fig. 1. The AES-curves (Fig. 1a) showing the behaviour of the intensity ratios of Yb NVV and Si LVV signals can be divided into five main parts. Within the *first*

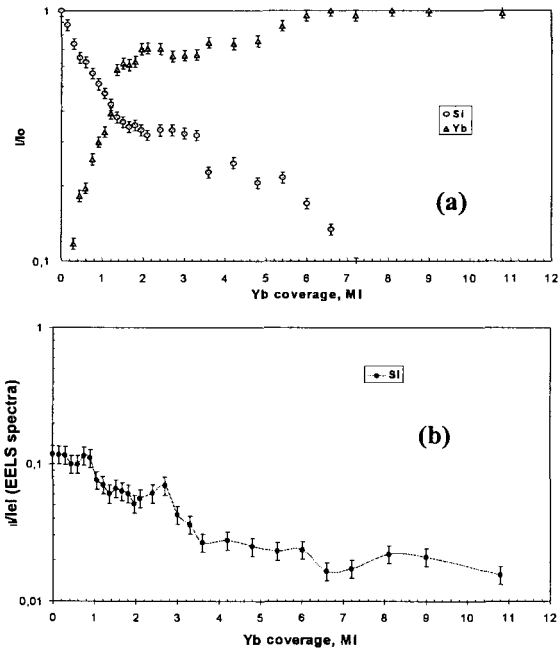


Figure 1. Intensity ratios of Si- LLV peaks and Yb- NVV peaks to their maxima (a) and intensity ratios of bulk silicon plasmon peak to its elastic electron beam peak (b) versus the Yb coverage.

implies the flat-layer growth mode.

Within the *second range* (1.35-2.2 ML) both Yb NVV and Si LVV intensity ratio curves (Fig. 1a) and EELS intensity ratio curve (Fig. 1b) display rather weak dependence on the Yb coverage. We suggest that the intermixing, silicon segregation on the topmost surface and formation of Yb two-dimensional silicide

range, which covers the range of 0.05-1.35 ML, two slopes of the AES-curves are observed. In the sub-range 0.05-0.6 ML, the Si LVV-signal decreases in the linear mode while the Yb signal displays a linear growth. The second coverage sub-range extends from 0.6 ML up to approximately 1.35 ML. Both Yb and Si AES-signals exhibit linear behavior but the slopes of the lines differ from that for the first region. In the EELS-intensity ratio of bulk silicon plasmons (Fig. 1b) the sharp decrease is observed, so masking of silicon atoms by Yb atoms increases. The linear dependence of both Yb NVV and Si LVV signals on coverage

determine the growth mechanism within this region of coverage. Behaviour of both Yb NVV and Si LVV signals (Fig. 1a) shows some signs of saturation within the coverage range from 2.2 ML up to 3.4 ML (*the third range*). In this coverage range the silicon bulk plasmon intensity (Fig. 1b) at first increases (2.2-2.7 ML) and then decreases (2.7-3.4 ML). We can suppose that the vertical-shaped silicide islands coalesce and change their shape in this range. Due to coalescence the islands become flatter in shape and the part of the Si surface which is covered with the growing film increases drastically.

The *forth coverage range* (3.6-6 ML) is characterized with saturation of the Yb NVV signal (at 6 ML), very slow gradual decrease of the Si LVV signal (Fig. 1a) and EELS intensity ratio (Fig. 1b). We attribute this behavior to a growth of Yb on silicide islands and some smoothing of the surface relief. At the coverage of 6 ML and higher (*the fifth range*) the Si signal begins to decrease and falls down to zero at the coverage of about 8 ML. It can be attributed to coalescence of Yb conglomerates and formation of a relatively thick and continuous Yb film. Surface morphology changes from flat to rough at Yb coverages more than 2 ML on Si(111) have been confirmed by AFM data.

The curves showing the Hall voltage (U_h (a)) and longitudinal voltage (U_p , (b)) for a Yb/Si(111)7x7 system versus Yb coverage (0.02-13.0 ML) are presented in Fig. 2(a,b). Their complex characters is attributed to the influence of the growth process on to the layer conductivity in the Yb/Si(111) system. The conductivity behavior relates to the evolution of morphological and electrical properties of the growing Yb (silicide, metal) film rather than to the changes within the space charge layer under the surface. Two-layer calculations [4] have shown that holes are majority carriers in the adsorbed Yb layer in all coverage range studied. Small sheet

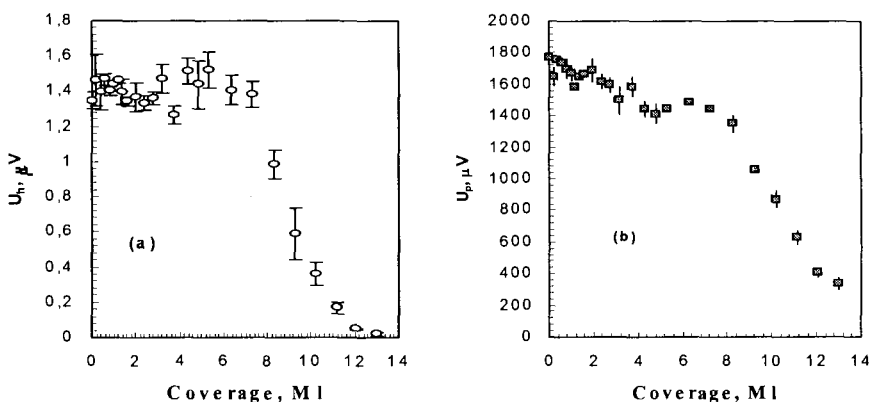


Figure 2. Hall voltage (U_h , (a)) and longitudinal voltage (U_p , (b)) as a function of Yb coverage on Si(111)7x7.

conductivity and high mobility were observed just for the first Yb layer (0.6 ML). Therefore, 2D conductivity channels exist at the first stage of Yb film growth on

silicon surface. We have suggested the formation of semiconductor with intrinsic character of conductivity in the first Yb layer on Si(111) surface. Some amplitude oscillations are observed in the coverage ranges 1.4-6 ML when formation of continuous Yb silicide film with metallic conductivity was observed. Similar oscillations were observed for the hole mobility and surface hole concentration dependencies on Yb coverage. The Yb metallic conductivity begins at layer thickness more than 8 ML, where the contribution of silicon substrate becomes already negligible. At Yb coverages higher than 13 ML continuous Yb film forms and nearly bulk-like metal conductivity is observed in the Si(111)/Yb system.

4 Conclusion

Conductivity oscillations have been observed during the interface formation in Yb/Si(111) system. We attribute these oscillations to evolution of morphological and electrical properties of the growing Yb film (2D Yb, silicide, near bulk metal) rather than to the changes within the space charge layer under the surface. Conductivity oscillations are explained by transition from semiconductor-type conductivity at the first growth stages (two-dimensional Yb growth) to metal-like conductivity of 2D and 3D Yb silicide films (different values).

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ANISOTROPY OF ENERGY SPECTRUM AND TRANSPORT PROPERTIES OF 2D CARRIERS IN UNIAXIALLY STRAINED GaAs/AlGaAs

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Numerical calculations, that have been performed, indicate a strong change of the 2D hole energy spectrum anisotropy in (001) p-GaAs/AlGaAs heterostructures under uniaxial stress along $\langle 110 \rangle$ directions. Experiments show that, in agreement with calculations, 2D hole mobilities μ in $[110]$ and $[1-10]$ directions reveal 2 times increase of their anisotropy $\mu_{[1-10]}/\mu_{[110]}$ at the uniaxial compression up to 5 kbar in $[1-10]$ direction and 2 times decrease under the stress applied along $[110]$. In (001) n-GaAs/AlGaAs the 2D electron mobility anisotropy changes not more than 10-15% and reflects only the 2D carrier density dependence of the anisotropic roughness scattering.

1 Introduction

Investigation of the influence of uniaxial compression on electronic properties of two dimensional (2D) electron and hole systems in (001)GaAs/Al_xGa_{1-x}As heterostructures seems to be very interesting both from fundamental and practical points of view. On the one hand, their magnetotransport characteristics are determined by the scattering processes, which are more or less common for the both types of the heterostructures. On the other hand, the energy spectra of 2D holes and 2D electrons transform in different ways under uniaxial compression due to the different symmetry of valance and conduction band states in GaAs/Al_xGa_{1-x}As.

2 Experimental

The n-(001)GaAs/Al_{0.3}Ga_{0.7}As and p-(001)GaAs/Al_{0.5}Ga_{0.5}As heterostructures were grown by molecular beam epitaxy on (001)GaAs semi-insulating substrates and doped in active layer with Si or Be, correspondingly. In all heterostructures only the ground state subband is populated. Samples of size $0.5 \times 0.8 \times 3.0 \text{ mm}^3$ with their long axis parallel to one or the other of the two directions $[110]$ and $[1-10]$ were cleaved from the structures along natural cleavage planes. Two identical, but mutually perpendicular, Hall-bar mesas were wet etched in the central part of the samples in

order to measure mobilities $\mu_{[1-10]}$ and $\mu_{[110]}$ along [1-10] and [110] directions in same experiment (we mark by S1 the mesa with its long dimension (450 μm) the parallel to the long dimension (3.0 mm) of the sample, and by S2 the mesa perpendicular to the mesa S1). In-plane uniaxial compression P up to 5 kbar was applied in the direction of the long dimension of the samples.

The sheet resistance R_{sq} for the two directions [1-10] and [110] was measured at 4.2 K for a number of samples from each structure. Shubnikov-de Haas (SdH) oscillations and Hall effect were measured at 1.4÷4.2 K in magnetic fields up to 6 T in order to determine carrier densities N . No significant difference between the carrier densities of the two mesas in all samples was observed neither at $P=0$ nor under compression (Fig. 1a, Fig. 2a). Therefore, the anisotropy of the resistance can be fully ascribed to anisotropy of the corresponding mobilities. The mobilities in [1-10] and [110] directions were found as $\mu_{[1-10]}=1/(NeR_{sq,[1-10]})$ and $\mu_{[110]}=1/(NeR_{sq,[110]})$ correspondingly. The ratios $\mu_{[1-10]}/\mu_{[110]}$ at $P=0$ and at $P=3$ kbar as well as the characteristics of the samples are represented in Table 1.

Table 1. Characteristics of the samples (T = 4.2K).

	Structure			
	HCO218 p-type	HCO251 p-type	HCO452 p-type	HCO146 n-type
Number of samples	4	9	12	4
$N, 10^{11} \text{ cm}^{-2}$ ($P=0$)	9.8	7.6	2.8	3.4
$\mu_{[1-10]}, \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ ($P=0$)	4.7	3.5	7.4	90
$\mu_{[1-10]}/\mu_{[110]}$ ($P=0$)	1.64 ± 0.10	1.47 ± 0.05	1.35 ± 0.06	1.28 ± 0.05
$\mu_{[1-10]}/\mu_{[110]}$ ($P_{[1-10]}=3 \text{ kbar}$)	3.4	3.4		1.46
$\mu_{[1-10]}/\mu_{[110]}$ ($P_{[110]}=3 \text{ kbar}$)		0.47	0.62	

3 Results and discussions

Without uniaxial compression the mobilities in the both types of samples are more high in the [1-10] direction. At 4.2 K the ratio $\mu_{[1-10]}/\mu_{[110]}$ varies in the interval 1.2 ÷ 1.6 for different heterostructures (Table 1). There is some increase of the anisotropy with increasing carrier density. This result is in agreement with the well-known concept of interface roughness scattering [1] that is determined mainly by chemical difference between the (110) and (1-10) planes in zinc-blend structures.

The values of mobility anisotropy are very similar for n- and p-type samples with close carrier concentrations. This confirms the assumption that the effect of interface roughness scattering, that is responsible for the mobility anisotropy at $P = 0$, is identical for n-type and p-type heterostructures.

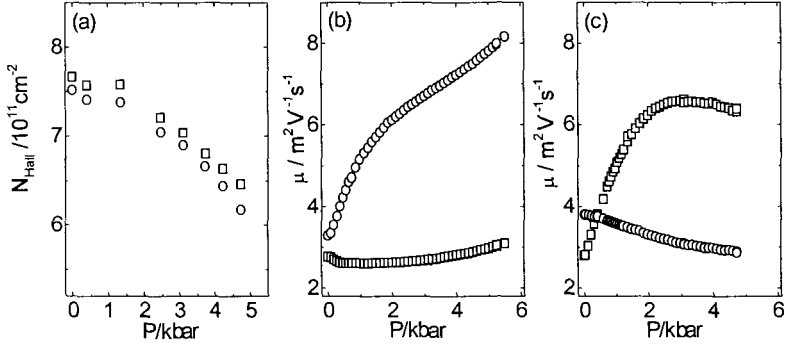


Figure 1. Pressure dependence of the hole concentration for p-GaAs/Al_{0.5}Ga_{0.5}As: mesa S1 – squares, S2 – circles (a). Pressure dependence of hole mobility in p-GaAs/Al_{0.5}Ga_{0.5}As for directions [011] (squares) and [0-11] (circles) under uniaxial compression along [110] (b) and along [1-10] (c).

Strong difference in the mobility anisotropy of 2D electrons and 2D holes arises under uniaxial compression. If uniaxial compression is applied the 2D hole mobility in p-type samples always increases in the direction parallel to the compression (mesa S1), and it decreases in the direction perpendicular to the compression (mesa S2) for the both directions of compression while the pressure dependence of the hole concentration is the same for S1 and S2 mesas (Fig. 1). As a result, under the compression along [1-10] direction the mobility anisotropy monotonically increases and the value $\mu_{[1-10]}/\mu_{[110]}$ can show twice increase in respect to the initial magnitude. For a compression, the ratio $\mu_{[1-10]}/\mu_{[110]}$ along [110] direction decreases and drops up to the value 0.5 at $P = 4\div 5$ kbar. This behavior is found to be in a qualitative agreement with the recent calculations of energy spectrum of 2D holes in p-(001) GaAs/Al_xGa_{1-x}As heterostructures under in-plane uniaxial stress [2]. These calculations indicate the strong change of the anisotropy of the hole Fermi surface that determines the anisotropy of mobilities in p-type heterostructures under compression. According to Ref. [2], the Fermi surface becomes oval shaped under the uniaxial compression with the longest dimension, i.e. the heaviest mass and the smallest mobility, just in the direction perpendicular to the direction of compression.

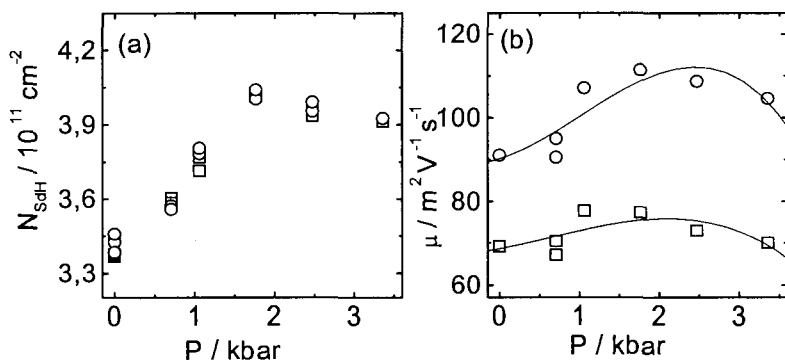


Figure 2. (a) Pressure dependence of the electron concentration for n-GaAs/Al_{0.3}Ga_{0.7}As: mesa S1 – squares, S2 – circles; (b) Pressure dependence of electron mobility in n-GaAs/Al_{0.3}Ga_{0.7}As for directions [011] (squares) and [0-11] (circles).

In n-type samples $\mu(P)$ dependencies for mesas S1 and S2 are similar and qualitatively follow the pressure dependence of N (Fig. 2). There is no evidence for drastic change of the anisotropy of the electron Fermi surface under uniaxial compression. The slight increase of the ratio $\mu_{[1-10]}/\mu_{[110]}$ (about 10%) reflects only the dependence of roughness scattering on the carrier concentration [1].

Acknowledgements

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THE PHOTON-ASSISTED TRANSPORT IN MESOSCOPIC DEVICES

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We analyze theoretically the phenomenon of photon-assisted quantum transport in superconductor(S)- semiconductor(N) mesoscopic system. Sub-gap structures in the I-V characteristics could be explained by multiple Andreev reflections. The electrical properties are strongly determined by the interface between superconductor and semiconductor. The current - voltage characteristics were found to be very sensitive to the photon frequency.

1 Introduction

Electrical properties of junctions formed between superconducting material, S, and a non-superconducting metallic material, N, which may be a metal or a degenerate semiconductor, are determined by special boundary conditions. If we consider a superconductor-semiconductor (S-N) interface with high transparency, a proximity effect is observed due to injection of electron pairs (Cooper pairs) from the superconductor into the semiconductor where they decay over a characteristic length, the induced coherence length.

In recent years, much attention on the transport properties of mesoscopic devices has been focused on the quantum effect [1]. Such devices are made of very clean 2DEG-sample [2] and with a finely structured split gate on top of the electron gas.

Many experiments [3,4] show that transport properties of superconductor(S)-semiconductor(N) junctions depend on the surface condition of the semiconductor layer. The results obtained from the study of transport characteristics of the S-N-S junctions show that these junctions are very promising as they work at low power loss and high switching speed. Many authors [5,6] studied the ballistic transport of electrons under the effect of a coherent far-infrared radiation.

In the present paper, a sandwich type model for the transport characteristics of the S-N-S junction is developed. The role of the Andreev reflection at the S-N interface is taken into account. We analyze the photon-assisted transport process due to both *intersubband* transitions (when the radiation field is in that transverse polarization) and to *intrasubband* transition (when the ac field is in the longitudinal polarization).

2 Theoretical treatment

The transport characteristics of S-N contact are influenced by two scattering processes [7], namely, normal tunneling and Andreev scattering [8].

We are going to derive an expression for the normal tunneling current as follows. The S-N-S junction behaves [9] like SINIS junctions, where S, I, and N denote a superconducting, insulating and normal metal layer, respectively. The insulating barrier plays as a Schottky barrier forming an interface between the superconductor and semiconductor. The current density, J_1 , for the transmitted electrons through the barrier is given by [10]:

$$J_1 = C \int \Gamma(E + n\hbar\omega) [F(E) - F(E - eV_o + n\hbar\omega)] dE, \quad (1)$$

where C is the proportionality constant, $F(E)$ is the Fermi-Dirac distribution function, V_o is the applied voltage, e is the electronic charge, ω is the frequency, $\hbar$ is Planck constant, n is an integer and $\Gamma(E + n\hbar\omega)$ is the tunneling probability of an electron through the Schottky barrier. This tunneling probability is determined by the WKB method [1]:

$$\Gamma(E + n\hbar\omega) = \exp\{(-2/\hbar) \int [2m^*(U(x) - E + n\hbar\omega)]^{1/2} dx\}, \quad (2)$$

where E is the total energy of the incident electron on the interface, and $U(x)$ is the potential energy of the transmitted electrons through the barrier. This potential, $U(x)$, can be modeled near the interface, under the effect of photon field of frequency, in a case when the semiconductor layer is of mesoscopic size [2] and expressed as:

$$U(x) = 2\Delta + eV_b - \sqrt{2e^3 N_d (V_b - V_o) x^2 / \epsilon} \quad (3)$$

In eq. (3), for simplicity, we shall assume that the pair potential, Δ , equals to the energy gap of the superconductor, V_b is the Schottky barrier height, N_d is the semiconductor doping density, ϵ is the permittivity of the semiconductor. Now, by substituting eq.(3) into eq.(2) and integrating we get

$$\Gamma(E + n\hbar\omega) = \exp\left[-\frac{\sqrt{2m^*}}{\hbar} \{eV_b + 2\Delta + n\hbar\omega - 0.5\sqrt{2e^3 N_d (V_b - V_o) / \epsilon - E}\}^{0.5}\right] \quad (4)$$

Eq. (4) shows the dependence of the tunneling probability, $\Gamma(E)$, on the parameters V_b , N_d , ϵ , the distance between two electrodes d and frequency ω , which are characterized the interface and the type of a semiconductor sandwiched between two superconductor electrodes. However, the current density, J_1 , for the transmitted electrons through the barrier will be obtained after substituting eq. (4) into eq.(1) and performing the integration, we get:

$$J_2 = C \left\{ \exp \left[-\frac{\sqrt{2m^*}}{\hbar} \{ eV_b + 2A + n\hbar\omega - 0.5d\sqrt{2e^3 N_d (V_b - V_o) / \varepsilon - E} \}^{0.5} \right] \times \right. \\ \left. [k_B T \ln \left[\frac{k_B T - E_F + E}{k_B T - E_F + E + n\hbar\omega + eV_o} \right] - [eV_b + 2A + n\hbar\omega - 0.5d\sqrt{2e^3 N_d (V_b - V_o) / \varepsilon - E}] \times \right. \\ \left. \ln [2k_B T - E_F + E + n\hbar\omega + eV_o] \right]_0^{E_m} \Bigg\}, \quad (5)$$

where $C = (e\hbar/Am^*)$, A is the area of the interface and the k_B is the Boltzmann constant.

The Andreev reflection is the second-order quantum mechanical process by which an electron-like particle incident on a superconductor with a quasi-particle excitation energy E above the Fermi energy may be transmitted as a Cooper pair in the superconductor, if a hole-like particle ($-E$) is reflected along the path of the incoming electron [12]. For a superconductor-semiconductor interface with low contact resistance (high transparency) and with a negligible Schottky barrier, the Andreev scattering leads to an increased conductance.

The current density, J_2 , due to Andreev reflection processes is given by [17]:

$$J_2 = (1/AeR_n) \int A(E) [F(E) - F(E - eV_o)] dE, \quad (6)$$

where $R_n = (1 + 2Z^2)R_o$, and $R_o = [2Ae^2 v_F N(0)]^{-1}$, in which Z , A , v_F , and $N(0)$ represent, respectively, the dimensionless scattering parameter which models the elastic scattering at the S-Sm interface, the cross-sectional area of the interface, the Fermi-velocity, and the density of states at the Fermi energy. The parameter $A(E)$ represents the probability of the Andreev reflection at the S-N interface and is given by [8]:

$$A(E) = [2(E^2 - \Delta^2)^{1/2}] / [E + (E^2 - \Delta^2)^{1/2}]. \quad (7)$$

It might be seen that this expression for $A(E)$ gives a quite fair description for the process of Andreev reflection occurring at the junction interface. Substituting eq. (7) into eq. (6) and performing the integration we get:

$$J_2 = (eV_o / AeR_n \Delta^2) \left\{ k_B T \ln \left[\exp[(eV_o - 2E_F) / k_B T] - 1 \right] \cosh(E_F / k_B T) + \right. \\ \left. (\exp[(eV_o - 2E_F) / k_B T] + 1) \sinh(E_F / k_B T) \right] + (E^2 - \Delta^2)^{0.5} + \\ \left. 2k_B T [\exp(E_F / k_B T) - \exp((eV_o - E_F) / k_B T)] \right\}. \quad (8)$$

3 Numerical calculations

We have calculated the total current density, J (eqs. 5,8), considering tunneling as a stochastic process. The values of maximum energies, E_m (eq. 5), of tunneling electrons have been varied as a random variable and we calculated the values of E_m

by Monte Carlo technique. Also, the calculated barrier height $V_b = 0.517$ eV was found to be in good agreement with [1,13].

Fig. 1 exhibits sub-gap structures in the I-V characteristics. A sub-gap structure can be explained by multiple Andreev reflections [8] at the interface between the semiconductor and the superconductor [7,12,13], where an electron in the semiconductor can be transmitted as a Cooper pair into the superconductor if a hole is reflected along the time-reversed path of the electron.

Fig. 2 shows the decrease of the current, J , as the temperature, T , increase when

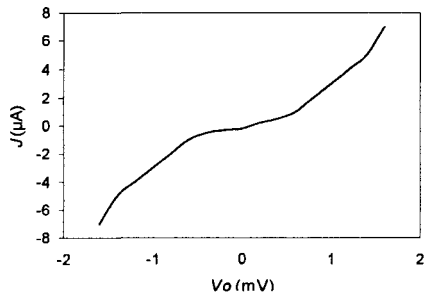


Figure 1. I-V characteristic of the junction (Nb-Si-Nb).

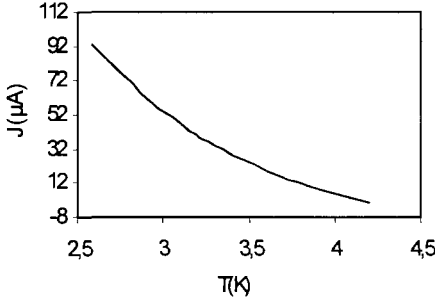


Figure 2. Temperature dependence of the current for (Nb-Si-Nb) junction.

the Schottky barrier was considered [13]. This variation shows that Josephson effect is observed at very low T . Fig. 3 shows the variation of the current with temperature, T , when the interface is transparent [16,17]. Our theory fits nicely the available experimental results [13,17,18]. The behavior of the total current density in eqs.(5,8) for the device irradiated with photons of different frequencies is shown in Fig. 4. The current is enhanced by this photon assisted process with different photon frequencies.

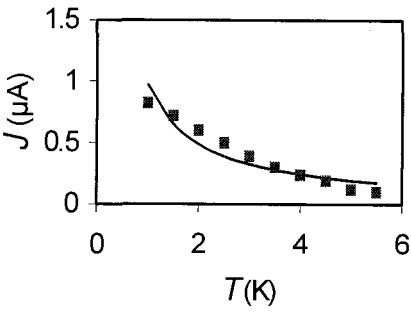


Figure 3. Temperature dependence of the current for (Nb-InAs-Nb) junction.

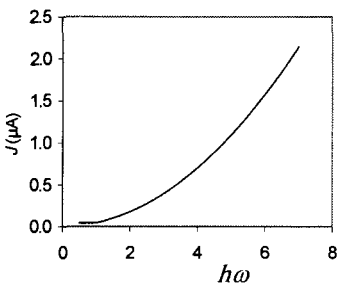


Figure 4. Photon energy dependence of the current.

4 Conclusion

Good agreement between the calculated and the measured curves leads us to the conclusion that photon-assisted transport is observed in S-N-S junctions with an enhanced current density. Our formula obtained could give a general sight about the quantum characteristics of the S-N junction. The effect of the photon-assisted quantum transport can be utilized to develop a very high frequency detector in the range of THz.

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ELECTRON BEAM SCATTERING FROM POTENTIAL FLUCTUATIONS IN A TWO-DIMENSIONAL ELECTRON GAS

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A numerical analysis, based on a Green's function approach, has been carried out to explain the interference patterns of an electron beam injected and detected via quantum point contacts. The calculations show the profound influence of back-scattering from potential fluctuations located close to the injector or detector on the transmission probability of the propagated electron beam. The interference patterns are sensitive to even small changes of the scatter location.

1 Introduction

Spatial correlations between randomly distributed charged donors in the remote layer of selectively doped GaAs/Al_xGa_{1-x}As heterostructures lead to smoothing of potential fluctuations in the underlying two-dimensional electron gas (2DEG) [1, 2]. This results in a reduction of electron scattering, i.e. an increase of the electron mobility at low temperatures. Recently, it has been demonstrated that an electron beam injected and detected via quantum point contacts (QPC) can be used as a sensitive local probe of the potential fluctuations in a 2DEG. The magnetic field dependence of the detected signal reveals interference patterns [3], which are associated with electron density inhomogeneities in a 2DEG. In another experiment, the strong influence of the scattering potential on electron beam propagation was demonstrated by means of an atomic force microscope [4].

Here we present a quantum mechanical model to calculate the experimentally observed interference patterns [3, 5]. We include two-dimensional potential fluctuations, temperature effects as well as the back-scattering from the potential fluctuations. The latter effect alters the interference patterns strongly when the scattering center is located close (within the phase coherence length) to the sample boundaries. Constructive and destructive interference arise when the position of the scattering potential in the direction of the detector QPC is changed by 1/4 of the Fermi wavelength.

2 Modeling of the electron beam experiment

The model we developed describes the ballistic propagation of electrons in a device as schematically presented in Fig. 1a. Two opposite QPCs are defined electrostatically in the 2DEG by externally controlled Schottky gates (gray areas).

Their conductance is set to one conducting mode. The distance L between injector and detector and the width W of the QPC exit are $4\text{ }\mu\text{m}$ and 100 nm , respectively, corresponding to the experimental situation. The QPC injects a collimated electron beam Ψ_0 into the 2DEG. In the model the restricted extension of the injected wave function Ψ_0 to the width W accounts for this effect. The injected electron beam is deflected in the presence of a weak magnetic field applied perpendicular to the 2DEG plane. The wave function of the propagating electrons can be determined using the Green's function method described in Ref. [5]. This wave function is perturbed by the scattering potential. We approximate the shape of scattering centers by a hyperbolic function and describe them by the following parameters: location (x_i and y_i), extension in the x - y plane (Δx_i and Δy_i), and potential height (V_0) [Fig. 1b)]. The height V_0 can be positive and negative, corresponding to regions of reduced and increased electron density in a 2DEG, respectively. Here, we limit ourselves to circular impurity potentials ($\Delta x_i = \Delta y_i$), which turned out to be sufficient to give a good agreement with experimental data.

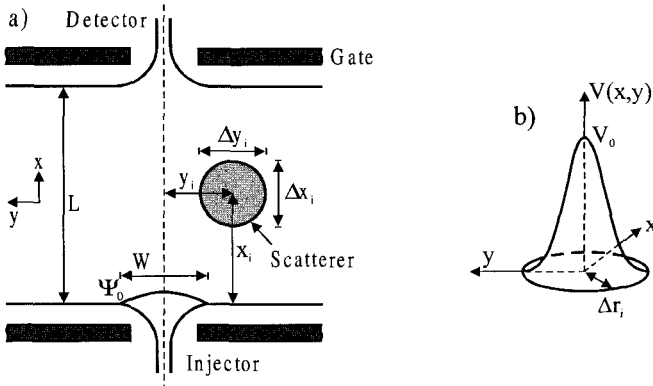


Figure 1. Scheme of the sample structure (a) and the shape of the scattering potential (b) used for the calculations.

The model includes the influence of the temperature. The contribution of the electrons with different energies $E_F \pm k_B T$ propagating from the injector to the detector (thermal broadening), as well as dephasing effects due to electron-electron scattering are taken into account. A comparison of the calculated transmission probabilities with the measured electron beam profile gives information about parameters of the scattering centers (height, size and location) [7].

For an adequate description of the electron beam propagation the effect of back-scattering is also taken into account. Electrons propagating in the direction of the detector can be subjected to multiple reflections by the potential fluctuations and the sample boundaries before they reach the detector QPC. When the length of their trajectories is smaller than the phase coherence length these electrons influence the observed interference patterns strongly. For the structure under consideration this

condition is met when the scattering center is located close to the injector or detector QPC.

If the impurity is located in the vicinity of the injector QPC an electron beam reflected back from the scattering potential towards the injector QPC modifies an injected electron beam Ψ_0 . Self-consistent calculations of the propagated wave function are required to take this effect into account.

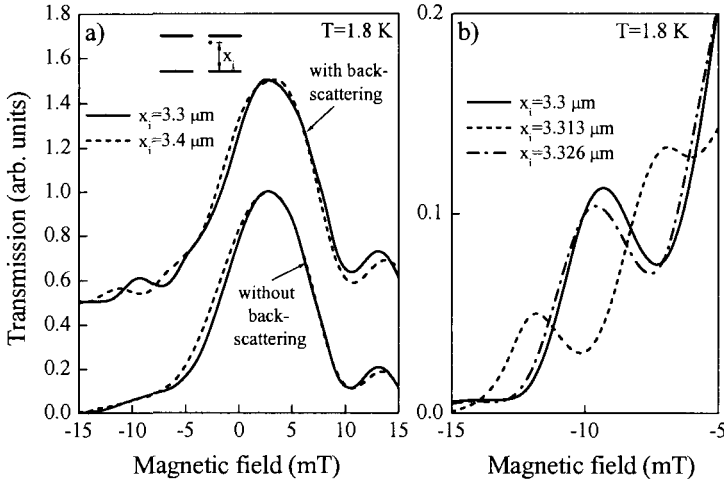


Figure 2. a) Calculated transmission probability without and with consideration of the back-scattering (the results considering back-scattering are displayed with a shift). Parameters for the scattering potential are: $x_i=3.3\ \mu\text{m}$ (solid lines) and $x_i=3.4\ \mu\text{m}$ (dashed lines), $y_i=0.15\ \mu\text{m}$, $\Delta r_i=0.075\ \mu\text{m}$, $V_0\approx 41\ \text{meV}$. b) Enlarged section of the upper trace in Fig. a) for three different values of x_i : $3.3\ \mu\text{m}$ (solid line), $3.313\ \mu\text{m}$ (dashed line), $3.326\ \mu\text{m}$ (dot-dashed line).

If the scatterer is located near the detector QPC, the influence of back-scattered electrons on the injected wave function is negligible and the self-consistent approach is not needed. The back-scattered beam can be determined as that part of the propagated wave which is transmitted to the boundaries of the sample near the detector QPC, from where it is reflected back towards the impurity and then back-scattered into the detector. In Fig. 2a the calculated transmission probability for two different positions x_i of the scattering potential with (upper curves) and without (lower curves) back-scattering effects are presented. Obviously, the tails of the signal are strongly influenced by back-scattering effects, which are very sensitive to the exact location of the impurity potential. This is demonstrated more clearly in Fig. 2b, where the signals are presented for a small range of magnetic field. If x_i is changed by an amount of order $\lambda_F/4$ (where $\lambda_F\approx 50\ \text{nm}$ is the Fermi wavelength for this sample), the maxima in the interference pattern turn into minima, and vice

versa. The initial shape of the signal is recovered by changing x_i by $\lambda_F/2$. This effect can be understood as a constructive and destructive interference of the electron beam.

Thus, our model explains the experimentally observed interference patterns in terms of scattering events at the potential fluctuations. The consideration of back-scattering effects in the model makes it very sensitive to the position of the scattering centers [7]. The profile of potential fluctuations in a 2DEG plane can be extracted quite precisely from the calculations of experimental interference patterns.

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CORRELATION OF MORPHOLOGY AND ELECTRICAL CONDUCTION IN NANOSTRUCTURED PERYLENE PIGMENT FILMS

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Surface morphology and electrical conduction in laser beam deposited perylene based thin films were investigated. It is found that the peak-to-peak value of the surface relief significantly increases with an increase of the substrate temperature at the deposition. Measuring of electrical properties by cyclic thermal desorption method shows that the hopping conductivity mechanism is realized in the films. The conductivity is intrinsic or impurity depending on the concentration of the adsorbed oxygen.

1 Introduction

The perylene derivatives are n-type organic semiconductors. They are of great interest as components for organic electronics. In particular, films of perylenetetracarboxylic diimide derivative (PTCDI) are used as n-layers in heterojunctions of organic solar cells [1]. The industrial application of these materials is now limited by insufficient knowledge about conductivity mechanisms and their correlation with structural features of the films.

In this paper, we compare experimental data on morphology of the vacuum deposited PTCDI films and their electrical conduction. As known [2], the conduction of PTCDI films is strongly influenced by adsorption of the atmospheric oxygen. Therefore, the measured absorbed oxygen concentration dependencies of conductivity, activation energy and tunnel factor are represented and then compared with the theoretical calculations based on the two-level model of the hopping conductivity [3].

2 Methods

The PTCDI films with thickness of 100 nm were prepared by laser evaporation in vacuum of 10^{-2} Pa. The LGN-703 infrared CO₂-laser with output power of 40 W was used for evaporation of powdered PTCDI target. The products of evaporation were deposited onto the glass-ceramic and mica substrates at 20°C (cold) and 150°C (hot). The glass-ceramic substrates contain a preliminary formed interdigital system of nickel electrodes.

Morphology of the films was investigated using AFM FemtoScan-Online (Advanced Technology Center, Moscow State University). The optical spectra in visible range were measured using spectrophotometer SPECORD-M40 (Carl Zeiss Jena). The dc conductivity of the films on glass-ceramic substrates and its temperature dependence were measured by a V7E-42 electrometer (BELVAR, Minsk) by cyclic thermal desorption method [4].

The conductivity σ of PTCDI films depends on the temperature T as described by equation

$$\sigma = \sigma_0 \exp(-E_a / kT),$$

where σ_0 is the tunnel factor, E_a is the activation energy of conduction, and k is the Boltzmann constant. Using this expression and the aforesaid set of experimental temperature dependencies, it is possible to determine the conductivity σ and the parameters σ_0 and E_a corresponding to various concentration of adsorbed oxygen.

The two-level model of hopping conductivity allows calculating from the set of experimental data the fundamental microscopical parameters of hopping conductivity – the electron localization radius and the concentration of localization centers corresponding to the intrinsic and impurity states [3].

3 Morphology and structure of PTCDI films

Fig. 1 shows the contact mode AFM images of the surface of PTCDI films deposited onto the cold and hot mica substrates. The films on glass-ceramic substrates demonstrate the same morphology. The PTCDI films with thickness of

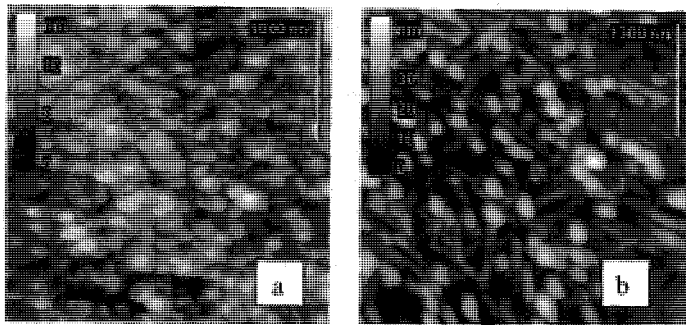


Figure 1. The AFM images of the surface of PTCDI films deposited on the substrates at 20°C (a) and 150°C (b).

100 nm have a polycrystalline structure with typical grains of 60–100 nm. The films deposited onto the hot substrates seem to have the greater peak-to-peak value of surface relief and the greater surface area of grain boundaries in comparison with its volume. Spectroscopic measurements show that the films deposited onto the both hot and cool substrates have coinciding absorption peaks at 478 nm and 570 nm. This fact demonstrates that both types of films have the same crystalline structure.

4 Electrical conduction properties

The measured dependencies of the conductivity, activation energy and tunnel factor on the concentration of adsorbed oxygen show that the hopping mechanism is realized in nanostructured PTCDI films. The main features of the electrical properties can be explained by means of Fig. 2, where x is the ratio of the adsorbed oxygen concentration to the full concentration of localization centers in the material. Lines A-A and B-B show the theoretical values for intrinsic and impurity

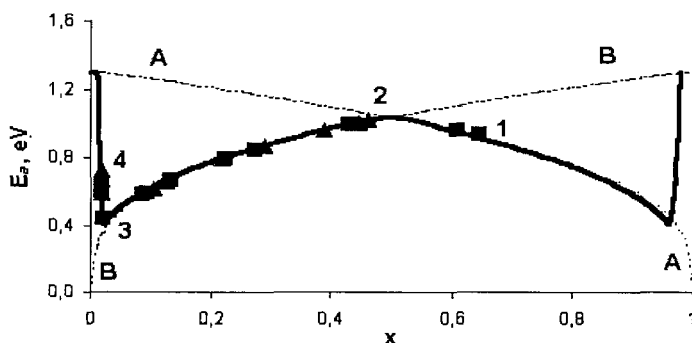


Figure 2. The dependence of conductivity activation energy on the relative concentration of adsorbed oxygen molecules.

conduction, respectively. More thick solid line corresponds to the calculated data for a two-component (PTCDI + oxygen) system. The experimental data for the films deposited onto the cold and hot substrates are marked by triangles and squares, respectively. The electron localization radius of intrinsic states is equal to 0.87 Å, and one of impurity states is equal to 0.90 Å at full concentration of localization centers of $3.3 \cdot 10^{21} \text{ cm}^{-3}$. At a high initial concentration of adsorbed oxygen (point 1), the conductivity is determined by the electron transport through the intrinsic states. As oxygen is desorbed, the amount of impurity states decreases while that of the intrinsic states accordingly increases. This leads to an increase in the activation energy (interval 1-2). At a critical oxygen concentration corresponding to point 2 the Fermi level is trapped at the impurity states and the electron transport through these states becomes dominating in the conductivity of

PTCDI films. Under this conditions, desorption of oxygen causes a decrease of activation energy (interval 2-3). Further decrease of adsorbed oxygen concentration causes the change in the conductivity type back from impurity to intrinsic one (interval 3-4).

5 Conclusion

Conductivity measurements of PTCDI thin films show that the films deposited onto cold and hot substrates have the same microscopic parameters of hopping transport whereas macroscopic values are different. The film on hot substrate has higher concentration of absorbed oxygen. No difference was found in the crystalline structure of the films. But the films significantly differ in surface morphology. The films on hot substrate are more porous and have significantly higher total area of grain boundaries. Therefore, the influence of oxygen on electronic properties of the PTCDI films is determined mainly by film morphology.

Acknowledgements

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EFFECT OF DOPING CONCENTRATION ON THE ELECTRON-PHONON COUPLING IN DEGENERATE SILICON FILM

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Electron-phonon coupling has been investigated in heavily doped silicon at subkelvin temperatures. The heat flow between electron and phonon systems is found to be proportional to T^6 . The coupling constant significantly increases with the increase of the electron concentration.

1 Introduction

Influence of the doping concentration on the electron-phonon coupling in silicon is an important issue for Si-based nanoscale devices. The electron-phonon coupling is weak at low temperature and electrons and phonons can attain different temperatures even when a small heat flow introduced into the system. In some circumstances, strong hot electron effects can restrain the operation of nanoscale devices, such as microbolometers and microcoolers.

In pure metals the electron-phonon interaction is inversely proportional to the number of thermal phonons $\tau_{e-ph}^{-1} \propto T^3$ [1]. This result is valid for pure limit: $q_T \cdot l \gg 1$ (q_T is thermal phonon wave vector, l is the electron mean free path) [2,3]. In dirty limit ($q_T \cdot l \ll 1$) electrons mostly scatter from defects and impurities and the electron-phonon interaction demonstrates more complicated behavior. According to the theoretical analysis made by Thouless [4] and Reizer [3] the relaxation time is proportional to T^4 ($\tau_{e-ph}^{-1} \propto T^4$) in the case of full phonon drag of scattering centers.

In present paper we report results of the electron-phonon coupling investigations in heavily doped silicon. The samples were silicon-on-insulator (SOI) films, which were heavily doped with phosphorous. The electron mean free path l_e is about 5 nm at low temperature in our Si samples [5] and velocity of sound $v_s = 5000$ m/s. The phonon wave vector is $q_T = k_b T / \hbar v_s$ and $q_T \cdot l_e = (0.13) \cdot T$, where

T is the temperature. This means that our system is in the dirty limit at subkelvin temperatures.

The dimensionality of the phonon distribution at low temperature may differ from 3D in thin films or layers. In our case we consider the acoustic mismatch between the film and the substrate to be negligible and therefore it is reasonable to assume that electrons interact with 3D phonons, and the electron-phonon interaction relaxation time τ_{e-ph}^{-1} is supposed to be proportional to T^4 .

The heat flow from electrons to phonons is described by a model [6], where electrons have heat capacity $C_e = \gamma T$ and the temperature change is described by

$$dP/dt = \tau_{e-ph}^{-1} C_e dT_e.$$

Substituting $\tau_{e-ph}^{-1} \propto T^4$, we obtain

$$P = \Sigma \Omega (T_e^6 - T_{ph}^6),$$

where P is the heat flow from electrons to phonons, Σ is a material-dependent electron-phonon coupling constant, Ω is the volume of the system and T_e (T_{ph}) is the electron (phonon) temperature, respectively.

2 Samples and thermometry

The samples were fabricated on a bonded SOI wafer with a 60-70 nm thick SOI film, where the buried-oxide layer was 400 nm thick. The wafer was heavily doped with phosphorous: $3.5 - 16 \cdot 10^{19} \text{ cm}^{-3}$. The electrons were uniformly heated in the very long (up to 1500 μm) SOI film by applying heating current between the contacts, which were at the ends of the silicon film. The Joule heat was calculated by using the values of the sheet resistance of the film and of the electrical current. A $^3\text{He}/^4\text{He}$ dilution refrigerator was used for the measurement in the temperature range between 50 mK and 500 mK.

The electron temperature was measured by superconductor-semiconductor-superconductor (S-Sm-S) junctions with Schottky barrier [7]. In the S-Sm-S structure the quasiparticle tunneling across the junction is very sensitive to the electron temperature in the normal electrode and it can be used as an electron temperature probe with negligible heat leak. Bias current used for electron temperature measurements was few orders of magnitude smaller than the current used for the electron heating in Si film and therefore the possible heating by the bias current can be neglected. The S-Sm-S thermometers used in experiments were calibrated against the ruthenium oxide thermometer (see inset in Fig. 1).

3 Results and discussion

The control of phonon temperature in electron-phonon coupling measurements is critical for a correct estimation of the electron-phonon coupling constant. In our experiment an additional electrically isolated S-Sm-S thermometer was placed near the Si film. Below 1K the electron-phonon thermal resistance in silicon is considerably larger than the Kapitza resistance between Si film and the silicon oxide layer, and therefore the S-Sm-S thermometer next to the silicon film was assumed to be at approximately the same temperature as the phonon system in the silicon film.

The measurements of the electron-phonon coupling constant in SOI films have been done at the substrate temperature between 100 – 500 mK. The heating current was swept slowly and the electron and phonon temperatures were measured simultaneously. The electron and phonon temperatures as functions of the heating power for the sample with $N_e = 12 \cdot 10^{19} \text{ cm}^{-3}$ are plotted in Fig. 1.

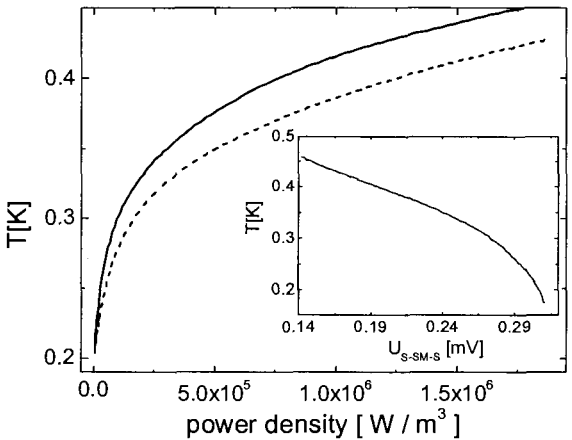


Figure 1. Electron (solid line) and phonon (dash line) temperatures for the sample with $N_e = 12 \cdot 10^{19} \text{ cm}^{-3}$ as a function of the power density applied to the electron system. Inset: calibration curve for a S-Sm-S thermometer.

The difference of the measured electron and phonon temperatures in the 6th power, i.e. $(T_e^6 - T_{ph}^6)$ was plotted against applied power density (see inset in Fig. 2) and from the slope of the graph we obtain the electron-phonon coupling constant Σ . The dependence is linear in this scale and it indicates that the heat flow between the electron and phonon systems has a T^6 -dependence. This corresponds to $\tau_{e-ph}^{-1} \propto T^4$ for the electron-phonon interaction relaxation time.

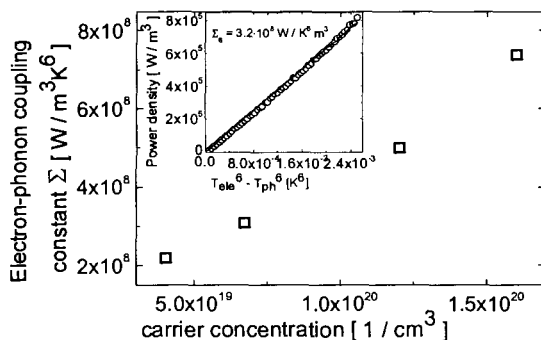


Figure 2. The electron-phonon coupling constant as a function of the carrier concentration. Inset: power density is plotted against $(T_e^6 - T_{ph}^6)$ for the sample with a doping level of $6.7 \cdot 10^{19} \text{ cm}^{-3}$. The electron-phonon coupling constant ($\Sigma = 3.2 \cdot 10^8 \text{ W/m}^3\text{K}^6$) is derived from the slope of the graph.

The electron-phonon coupling constant as a function of the doping level in silicon is presented in Fig. 2. The coupling is approximately directly proportional to the electron carrier concentration in the heavily doped silicon, but the electrical resistance of the silicon only slightly depends on the carrier concentration in this range. This can be used for optimization of thermal characteristics of different microdevices operating at low temperatures.

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CONDUCTION OF NANOWIRES FORMED BETWEEN METALLIC ELECTRODES

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The paper presents a study of nanowires formed dynamically between metallic electrodes. We examined nanowires produced in the contact of the following metals: Au, Cu, Co, Ni, W. Our measurements concern nanowires formed between both magnetic and nonmagnetic metals. It was noted that formation of nanowires is supported by using an electrode which is a good metallic electrical conductor for the contact, i.e. Au or Cu.

1 Introduction

Research on nanowires formed dynamically in the contact of two metallic electrodes was conducted. The electrodes made out of metals under examination are brought close and removed in cycles. During the last phase of bringing the electrodes close, just before the full contact, as well as during the last phase of removing them, just before the interruption phase, a structure with nanometer dimensions appears, called nanowire. Such method of forming nanowires was proposed by Costa-Krämer et al. [1]. The subject of our research was the electrical conductance of such nanowires. The quantum of electrical conductance changes is the G_0 constant, depending exclusively on fundamental constants of physics $G_0 = 2e^2/h \cong 12.9 \text{ k}\Omega$.

Even though the nanowire electrical conductance depends exclusively on its geometrical dimensions, and does not depend either on the type of metal or on temperature, the dynamic nanowire formation itself is different for different metals. In particular, the intensity of nanowire formation and the duration of the process are very strongly influenced by the type of metals used. The nanowires forming intensity is measured with statistical calculations of characteristic $G=f(t)$. The result of the calculations is a histogram.

2 Measuring system

The measuring circuit consists of a bias voltage supply V_s , a pair of macroscopic electrodes, which make up the quantum contact under examination, and a serial resistor R_p of 1000Ω as illustrated in Fig. 1. The voltage drop V_p on the resistor R_p is a function of the measured conductance G_w . The piezoelectric device is used to control the backward and forward movement of the macroscopic contacts, between which the nanowires occur. A high voltage amplifier, controlled by a digital

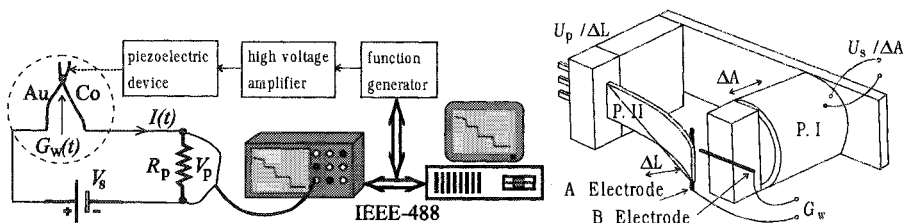


Figure 1. A system for measurements of conductance quantization: an electrical circuit (left) and a piezoelectric actuators (P I and P II) for precise moving of electrodes (right).

function generator, supplies the piezoelectric device. The measurements have been carried out in air at room temperature. The conductance was measured between two metallic electrodes, moved to contact by the piezoelectric tube actuator.

3 Conductance quantization in metallic nanowires

In a constriction of a metal with nanometer dimensions, called a nanowire, the ballistic transport of electrons occurs in conductive channels. The number of channels is proportional to the width of the nanowire. The conductance of such nanowire is described by Landauer's formula [2]:

$$G = \frac{2e^2}{h} \sum_{n=1}^N T_n,$$

where: e – electron charge, h – Planck quantum, T_n – electron transmission in channel number n .

We have examined the conductance quantization of nanowires for three non-magnetic metals (gold, copper and tungsten) and for two magnetic metals (cobalt and nickel). For nonmagnetic metals, the conductance quantization in units of G_0 was previously observed. The quantization of conductance in our experiment was also evident. All characteristics showed the same steps equal to $2e^2/h$. The characteristics are only partially reproducible; they differ in number and height of steps, as well as in duration. It should be emphasised that quantum effects were observed only for some of the characteristics recorded. So far, the conductance quantization has been more pronouncedly observed for golden contacts. Fig. 2 shows exemplary plots of conductance versus time during the process of drawing a golden nanowire [3] and a copper nanowire.

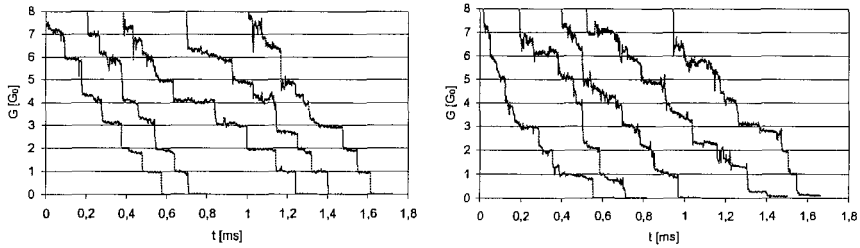


Figure 2. Conductance quantization in metallic nanowires: golden nanowires (left) and copper nanowires (right). The characteristics presented are chosen from 20000 consecutive measurements for both metals.

Time characteristics of golden and copper nanowires shown in Fig. 2 are shifted along the time axis in relation to the first characteristic in order to present clearly the consecutive 2nd, 3rd, 4th and 5th plots. Fig. 3 shows the conductance histogram obtained from 20000 consecutive characteristics for each pair of electrodes formed by Au, Cu, Co, Ni, W (the bias voltage $V_{bias} = 0.43$ V).

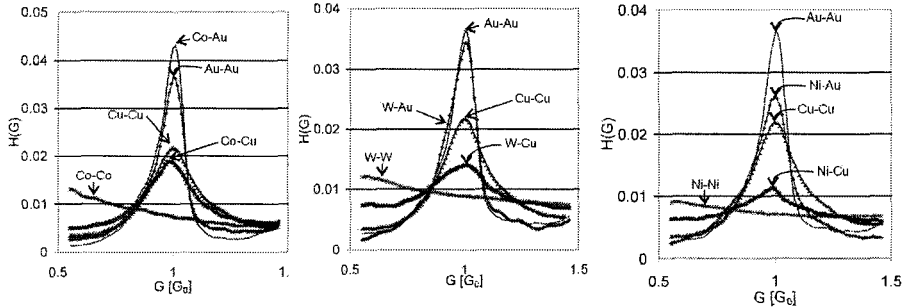


Figure 3. Conductance histograms obtained from conductance characteristics of nanowires: a) nanowire formed by cobalt and Au or Cu; b) nanowire formed by tungsten and Au or Cu; c) nanowire formed by nickel and Au or Cu

From 20000 consecutive conductance characteristics $G_w = f(t)$ for one pair of metals, we calculated a histogram of quantization in the conductance range from 0.6 to $1.3G_0$. The characteristics in Fig. 2 and Fig. 3 were drawn after diminishing the contact conductance by the so called residual conductance. We have measured the conductance of nanowires formed by the following pairs of magnetic and nonmagnetic metals: Co-Co, Ni-Ni, W-W, Au-Au, Cu-Cu, Co-Au, Co-Cu, W-Cu, W-Au, Ni-Au, Ni-Cu. For magnetic metals (Ni, Co) and for W we can observe some steps with a high of $2e^2/h$ on the conductance characteristics but no peaks on the histograms – Fig. 3. This histogram for Ni, Co and W nanowires looks quite differently from the histogram for Au and Cu nanowires. It may be stated that the nanowires formed out of a contact in which at least one electrode is a good electrical conductor (Au, Cu), occur more frequently and are more stable (have a longer duration).

We found also that the sharpness of the histogram curve depends on the speed of moving electrodes (macroscopic wires) during formation of a nanowire. Each histogram presented in this paper was obtained at a speed of 4.8 $\mu\text{m/s}$.

4 Discussion

The conductance quantization has proved to be observable in an experimental set-up, giving opportunity to investigate quantum effects in electrical conductivity. The curves of histograms from nanowires with an electrode of cobalt, nickel or tungsten do not contain peaks. In our opinion, a curve of histograms without peaks for some nanowires can be caused by the hardness of magnetic metals [3].

Table 1. Hardness of investigated metals (in Brinell scale)

Metal	Au	Cu	Ni	Co	W
Brinell hardness [MPa]	180	400	850	1250	2500

Nanowires in soft metals are formatted more frequently. The quantization in good electrical conductor (Au, Cu) occurs more frequently and its histograms have peaks because of easier formation of nanowires from soft metals than from hard metals (Ni, Co, W). For a nanowire formed by a pair of metals, a soft metal and a hard one, the histogram is like the histogram of the softer metal. Probably the nanowire formed from such pair of metals contains mostly atoms of the soft metal. The study of the nanowires forming effect enables to allow for conductance quantization in electronic circuits containing mechanical contacts, e.g. relay contacts.

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OXIDIZED SILICON NANOCLUSTERS: A THEORETICAL STUDY

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Total energy calculations have been performed to understand the role of oxidation on the structural, electronic and optical properties of Si nanoclusters. Our aim is to explain the peculiar properties of aged porous Si samples, heavily oxidized Si nanoparticles and embedded Si nanocrystals. We have studied two types of structures: isolated H-covered clusters, replacing Si-H bonds with various Si-O bonds; and Si nanoclusters embedded in a SiO₂ matrix. Regarding the isolated clusters we find that the optoelectronic properties depend on the type and the number of Si-O bonds at the cluster surface. For the embedded systems our results show that a close interplay between chemical and structural effects plays a key role in the light emission processes.

1 Introduction

Silicon-based light-emitting materials, such as porous silicon and Si nanocrystals, have been intensively investigated because of the promising applications in advanced electronics [1,2]. Understanding the properties of these novel materials requires learning more about their structures. Passivated Si nanoclusters (NC) are the ideal theoretical model to this aim. Most of the calculations have used hydrogen as NC passivating agent, focusing mainly on quantum confinement effects. The huge discrepancies between calculated band gaps (E_g) for H-covered Si NC and experimental results on oxidized structures [3-7] have pointed out that also the chemistry of the surface can produce substantial impact on the Si NC properties. Moreover starting from H-covered samples, oxidation results in a saturation value for the PL energies almost independent from the size [4]. In this paper, we present Density Functional (DFT) calculations on Si NC of different sizes; we discuss the effects on the optoelectronic properties induced by the substitution of Si-H bonds with different types and numbers of Si-O bonds and the structural and optoelectronic properties of Si NC embedded in SiO₂.

2 Methods

Total energy calculations (GO) on isolated Si NC have been based on DFT in the local density approximation (LDA), using two different plane wave pseudopotential codes: the FHI98md [8] and the CASTEP [9]. Both norm conserving Martin-Troullier and ultrasoft pseudopotentials have been used, setting the cut-off energy at

680 eV and 380 eV, respectively. We have employed 3D periodic boundary conditions using large supercells to avoid interaction between repeated NCs. GO calculations on Si NC embedded in SiO₂ have been based on CASTEP [9] using a GGA-PBE XC treatment and peculiar ultrasoft pseudopotentials with a cut-off energy of only 265 eV. Optical properties have been obtained within LDA, considering direct transitions only. All the atoms have been allowed to relax, until the residual forces were less than 0.05 eV/Å.

3 Models and results for the Si nanocystals

We have considered Si NC of different diameters: Si₁₀ (0.5 nm), Si₁₄ (0.7 nm) and Si₃₅ (1.0 nm). We started with fully H-covered NCs and then we have progressively substituted H and Si with O, considering two types of Si-O: the Si-O-Si backbond and the Si=O double bond. In case of multiple oxidation, the presence of several, up to six, Si=O bonds has been considered. The presence of O atoms in backbond positions produces huge variation of the surface structure, whereas Si=O bonds cause only small local distortions. On the contrary, whereas the Si-O-Si bond does not affect too much the NC energy gap value (E_g), the Si=O bond results in a huge red shift of the fully H-covered related band gap, as witnessed by Fig. 1(a).

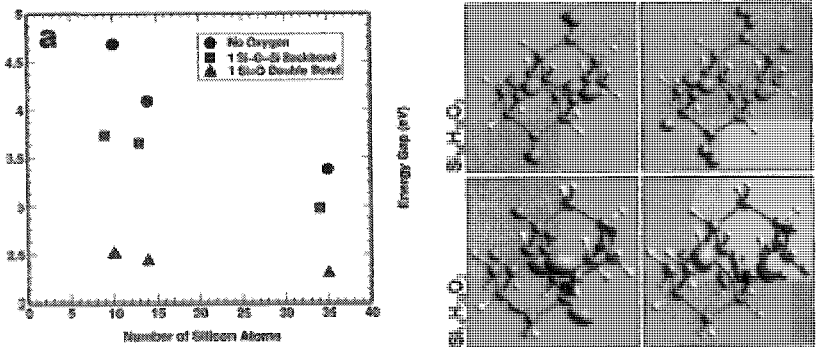


Figure 1. (a) E_g values as a function of NC size (Si atom number) for the different bond configurations. (b) Iso-surfaces of the square modules of the HOMO and LUMO Kohn-Sham orbitals for the Si₁₄H₂₀ NC in presence of Si=O bond (Si₁₄H₁₆O₂) or Si-O-Si (Si₁₄H₂₀O₂). O: black, H: white, Si.

The different behavior is due to the fact that the Si=O bond produces new states within the band gap, strongly localized on the O atom itself, whereas for the Si-O-Si this does not happen (see Fig. 1(b)). Moreover, the presence of Si-O-Si and Si=O bonds demonstrates that it is this last bond that dominates the optoelectronic properties. Increasing the oxygen coverage level, *i.e.* adding new Si=O bonds, the gap decreases. The reduction is not linear with the number of Si=O bonds (Fig. 2). For all the cluster sizes the strongest red shift occurs with the first Si=O bond; a second Si=O bond produces a further reduction but weaker than the first and the

more we add Si=O bonds the smaller their contribution becomes. A sort of saturation limit is reached. Since the HOMO-LUMO transitions are allowed our results reproduce the observed PL red shift for oxidized Si nanoparticles [4].

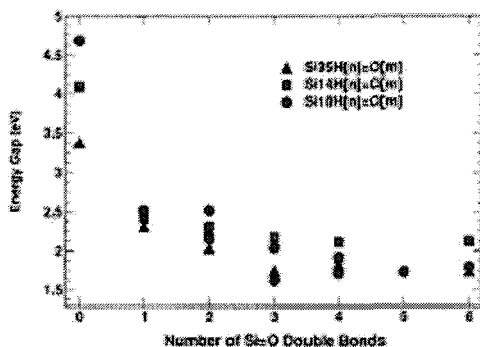


Figure 2. E_g values for the three Si NC as a function of the number of Si=O bonds at the surface.

Energy levels and total density of states for the multiple oxidation cases are shown in Fig. 3 for the Si_{14} clusters. An increasing number of Si=O bonds at the surface results in a directly proportional number of localized states which pile up at both band edges. This states accumulation can be at the origin of the observed large PL bandwidth for isolated Si single quantum dots [10].

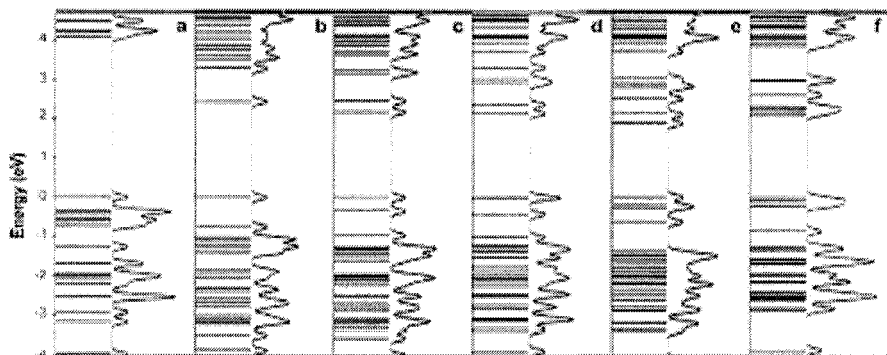


Figure 3. Energy levels and total density of states at Γ for the Si_{14} based clusters. From left to the right fully hydrogenated (a), with 1 (b), 2 (c), 3 (d), 4 (e) and 6 (f) double-bonded O atoms.

To model Si NC embedded in SiO_2 matrix we have built up a cubic supercell of SiO_2 β -cristobalite (BC) whose diamond-like geometry allows the drawing of simple Si-SiO₂ interfaces. Then we have cut out from the SiO_2 structure 12 O atoms and linked together the Si atoms left with dangling bonds. Thus, we have an initial supercell with 10 Si bonded together to form a small NC with highly strained bond length (+33%). We have then performed total energy calculations for relaxing the

structure finding that the Si NC has still crystalline-like geometry with only +14% strain; that the NC is surrounded by a shell of stressed SiO_2 of about 1 nm thickness; and that rest of the matrix remains unaltered. In the relaxed structure (Fig. 4(a)) the presence of non-dispersed states from the NC and from the interface shell (Fig. 4(b)) reduces the SiO_2 gap to the visible.

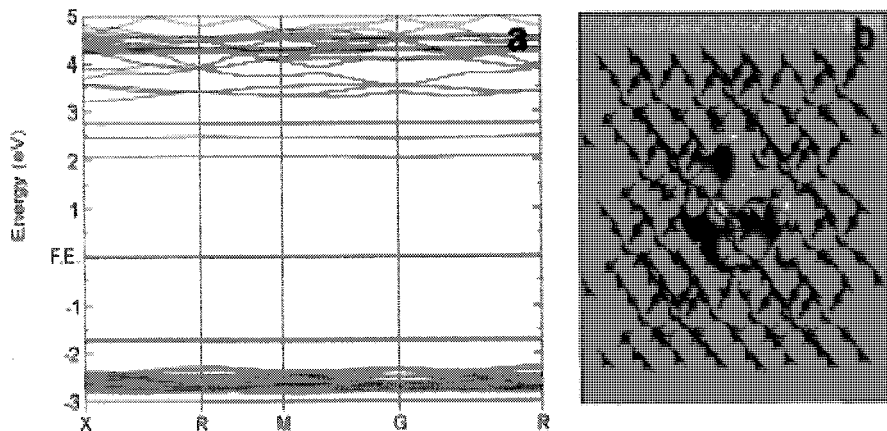


Figure 4. (a) Band structure for the Si NC embedded in SiO_2 . (b) HOMO isosurface; black: O atoms, grey: Si atoms in SiO_2 , with: Si atoms in Si NC.

These results agree with x-ray absorption fine structure measurements on Si nanocrystals dispersed in SiO_2 , that indicate an active role in the light emission process of both nanocrystals and interface region [11].

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ABOUT THE IMPURITY EFFECT IN THE $\text{SiO}_2\text{:nc-Si}$ SYSTEM

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Possible mechanisms of an impurity effect on the photoluminescence properties of the $\text{SiO}_2\text{:nc-Si}$ are summarized. The experimental data manifested the action of these mechanisms are presented. It is shown that, depending on the kind of the impurity, its concentration and annealing conditions, the enhancement or quenching of the photoluminescence associated with Si nanocrystals can be observed.

1 Introduction

Silicon nanocrystals embedded into the SiO_2 matrix ($\text{SiO}_2\text{:nc-Si}$) are promising in fabrication of light-emitting devices. One of the attempts to improve their luminescence properties is doping by shallow impurities. However, the results in this field are rather contradictory. So, in [1,2], it was established that phosphorus effectively enhances the photoluminescence (PL) of $\text{SiO}_2\text{:nc-Si}$ obtained by ion implantation. The same results were reported in [3] for the $\text{SiO}_2\text{:nc-Si}$ fabricated by co-sputtering method. At the same time, it was observed in [4] the PL weakening under the phosphorus doping. The root of such a contradiction is the existence of many mechanisms of impurity effect in QD, in particular for the case of $\text{SiO}_2\text{:nc-Si}$ system. In this paper we attempt to summarize the mechanisms and to discuss their role for several examples of original experiments.

2 Possible mechanisms of the impurity effect

The following factors can influence luminescent properties of the $\text{SiO}_2\text{:nc-Si}$ system.

- (1) *The mechanical stresses* [3]. The stresses can be induced by the difference of densities and (or) thermal expansion coefficients of SiO₂ and Si. This can lead to the break of the bonds at the SiO₂/nc-Si interfaces and, hence, to the formation of nonradiative recombination centers. The impurities can enhance or, on the contrary, reduce the stresses and correspondingly enhance or weaken the luminescence.
- (2) *The passivation of the dangling bonds*. This mechanism is well known for hydrogen [5]. Donor impurities (such as phosphorus) can play the same role.
- (3) *The precipitation of impurity atoms or the formation of complexes with constituents of the system (Si, O)*. This can bring about local mechanical stresses and cause the effects pointed above. Alternatively, this can serve as the centers for the nucleation of the Si nanoinclusions and thus to affect their number and (or) sizes [6].
- (4) *The impurity-induced crystallization of amorphous nanoinclusions*. It was established that donor or acceptor impurities in Si can stimulate the near-room temperature crystallization [7]. It can increase the number of nanocrystals and enhance the luminescence. For the case of impurity implantation, the crystallization can also be caused by “shock” mechanism – at the interaction of the projectile with amorphous inclusions [8].
- (5) *The introduction of additional electrons in QD by donor impurity* [1,2]. It can provide an alternative way for radiative recombination, thus resulting in the luminescence enhancement.
- (6) *The impurity-induced enhancement of the non-direct transitions*. This is purely quantum effect considered in [9].
- (7) *The Auger recombination* [10]. It leads to the decrease of the probability of radiative transitions and, hence, to quenching the PL.

3 The experimental

Thermally grown SiO₂ films (0.3-0.6 μm thick) were used as the starting materials. Si⁺ ions were implanted at energy $E=140$ keV and dose $\Phi_{Si} = 1 \cdot 10^{17} \text{ cm}^{-2}$. Then, annealing in N₂ was performed at 1000°C or 1100°C for 2 hours. The films were implanted with P⁺ at $E=150$ keV, $\Phi_P = (0.1-300) \cdot 10^{14} \text{ cm}^{-2}$, by B⁺ at $E=60$ keV, $\Phi_B = (0.1-10) \cdot 10^{16} \text{ cm}^{-2}$, or by N⁺ at $E=70$ keV, $\Phi_N = (0.1-100) \cdot 10^{15} \text{ cm}^{-2}$. The ion current density was $\leq 3 \text{ μA/cm}^2$. The postannealing after doping was performed by two means – either the samples were annealed in one step at 1000°C or 1100°C, or at first, they were Si⁺ implanted and annealed at 1000°C or 1100°C, then doped with impurity and then step-by-step annealed at progressively rising temperatures (each step was 100°C and the temperature was kept constant for 0.5 hour). The PL was measured at room temperature under Ar⁺ laser excitation ($\lambda=488 \text{ nm}$).

4 Results and discussion

The influence of phosphorus doping on the PL of ion-implantation-produced $\text{SiO}_2\text{:nc-Si}$ is demonstrated in Fig. 1 [1,2,9,11]. The positive role of phosphorus can be explained by the action of the mechanisms (2), (5) and (6). The contribution of the mechanism (4) seems to be not probable because the order of annealing (nanocrystals formation) and P implantation in this case does not affect the degree of the impurity-induced enhancement. Note that the role of the Auger recombination (mechanism (7)) is not apparently revealed. It should be mentioned that the influence of the Auger recombination was considered only for impurity-free QD. For QD with donor atoms this consideration can occur to be not valid.

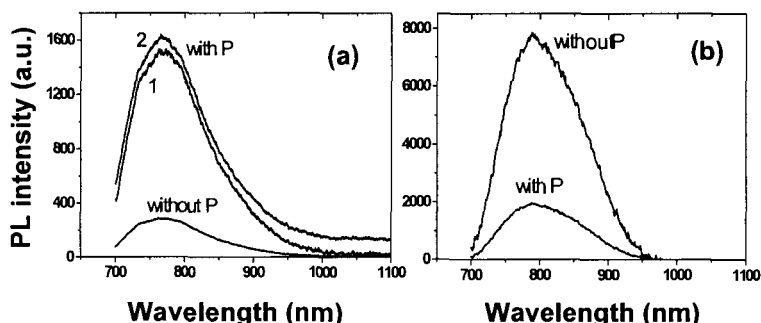


Figure 1. The influence of P doping on the PL of $\text{SiO}_2\text{:nc-Si}$ system formed at 1000°C (a) and 1100°C (b). In Fig. 1a the order of implantation and annealing: 1 – Si^+ , P^+ , annealing at 1000°C (2 h.); 2 – Si^+ , annealing at 1000°C (2 h.), P^+ , annealing at 1000°C (2 h.). $\Phi_{\text{Si}} = 10^{17} \text{ cm}^{-2}$, $\Phi_{\text{P}} = 10^{16} \text{ cm}^{-2}$.

The efficiency of various mechanisms essentially depends on the annealing conditions. So, in Fig. 1b the influence of phosphorus is shown for the same implantation conditions as in Fig. 1a, however, the formation of the system before P^+ implantation was provided at 1100°C. It is evident that P plays the quenching role. The difference in the role of phosphorus (Fig. 1a,b) can be explained by different effective sizes of nanocrystals obtained at 1000 and 1100°C. In addition, the role of mechanism (2) should be weakened by the decrease of broken bonds with the rise of the annealing temperature.

The role of the mechanism (4) can be illustrated by the following data. The exceeding of initial PL level at such small P^+ dose as $1 \cdot 10^{13} \text{ cm}^{-2}$ (Fig. 2a) evidences in favor of *in situ* “shock” crystallization (by P ions) of the nano-inclusions which have not yet been crystallized at 1100°C. The increase of PL at high P^+ doses (Fig. 2b) can be explained by the “high dose effect” [7].

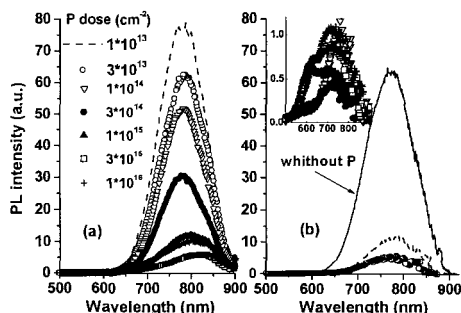


Figure 2. The PL spectra of $\text{SiO}_2\text{:nc-Si}$ system formed at 1100°C then implanted by P and step-by-step annealed at 1000°C (a) and as-implanted by P (b). $\Phi_{\text{Si}} = 10^{17} \text{ cm}^{-2}$.

For B^+ implantation, in accordance with the above mentioned reasons, we can expect weakening of PL. Boron facilitates an increase of the excess stresses and break the bonds. It strongly quenches the PL as seen in Fig. 3a, but the indication of “high dose effect” is seen, too.

Nitrogen has low solubility in Si and (as boron) large difference in the atomic radii with Si. Fig. 3b demonstrates dependence of the ratio of PL intensities with and without doping on the N^+ dose. It has complicated nonmonotonous character which can be explained by precipitation of N during formation of Si nanocrystals. The latter can cause two opposite effects: the enhancement of the mechanical stresses and the appearance of additional centers for the growth of Si nanocrystals. At low and high nitrogen doses the first factor prevails, whereas for the intermediate doses the second factor is revealed. (At low doses, evidently, the segregation of N on the growing Si nanoinclusions takes place).

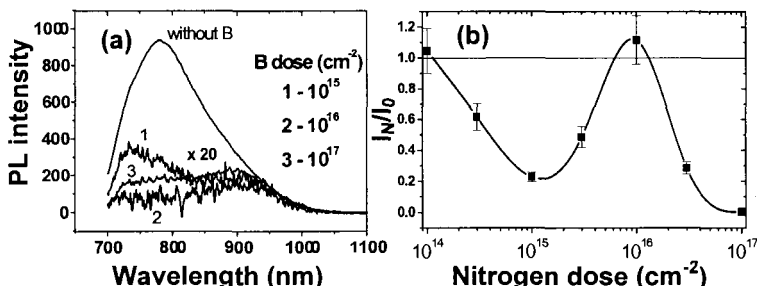


Figure 3. The PL spectra of $\text{SiO}_2\text{:nc-Si}$ system formed at 1000°C , implanted by B^+ and annealed at 1000°C (a). The influence of N doping on the PL intensity of SiO_2 films implanted by Si^+ , N_2^+ and annealed at 1000°C (b). $\Phi_{\text{Si}} = 10^{17} \text{ cm}^{-2}$.

5 Conclusion

Various mechanisms of an impurity influence on the SiO₂:nc-Si PL properties can exist. Depending on the kind of impurity its concentration, and annealing conditions, this influence can be either positive or negative. More theoretical and experimental study of the subject is important for ion-fabricated and other kinds of the SiO₂:nc-Si systems.

Acknowledgements

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COMPOSITE NANOSTRUCTURES BASED ON POROUS SILICON HOST

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In this paper we review different technological aspects of porous silicon (PS) utilization as a host material for the fabrication of composite nanostructures. Different types of PS host filling materials and final treatments (annealing, oxidation, and others) are analyzed.

1 Introduction

The technology of porous silicon (PS) has a unique propriety to control the sizes of the pores from a few microns to a few nanometers. Indeed, the realized PS keeps a perfect crystalline structure, has a huge surface and a high adsorption activity [1]. Many materials as elementary metals, semiconductors, bio-substances and living cells can be used to fill and/or coat the PS pores [2]. The capillary force helps the pores filling, while the silicon needles acts as catalyst activating polymerization [3] and reduction [4] reactions. High temperature treatment in different environment converts the PS structures in materials as SiO_2 , Si_3N_4 , SiC , or silicide [1]. Temperature and/or environment composition regulates the conversion degree of PS. All these factors provide a real possibility for the formation of different composite structures based on PS host. In this paper, different techniques that use the PS host as a suitable material for nanotechnology applications are reviewed.

2 Fabrication of PS based composite nanostructures

Technological process of the PS based composite structures is illustrated schematically in Fig. 1. The process starts with the PS host formation and then, if wanted, the modification of PS can be performed. The second step is filling the PS pores with a material or coating formation on the PS surface. The final step consists of different treatments (e.g. annealing, oxidation) to obtain a desired structure. The process sequence can be changed if filling materials are introduced into Si by ion implantation [5] before the porosification. Moreover, the process can be shortened if

the porosification and the introduction/deposition of the filling materials are performed simultaneously [6,7] by adding the substances in the anodizing solution.

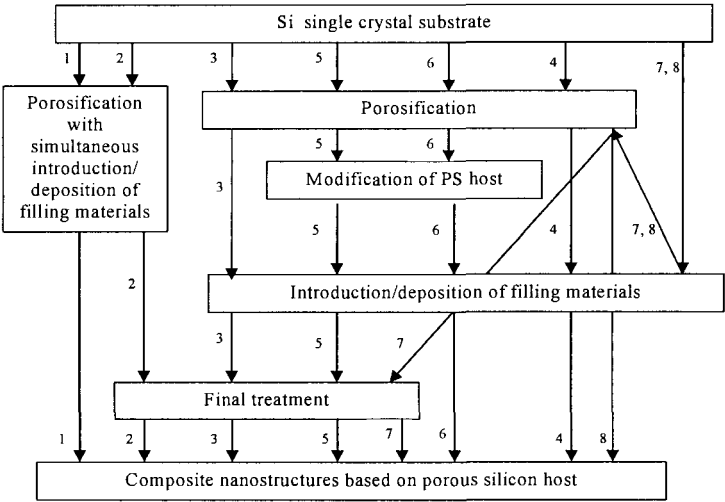


Figure 1. Technological process of PS based composite structures.

All the technological steps can be accomplished in different ways. Below, we consider general peculiarities of the above-mentioned technological steps.

2.1 PS host

The PS layer formed on a Si substrate is the most frequently used as a PS host. Sometimes, partial or complete modification of the PS layer (by annealing, oxidation, carbonization, etc.) is performed prior to pore filling or coating process [2]. Multi-layered PS structures (with different porosity) [8], self-supported PS films [9], and PS grains (PS layer separated from Si substrate and divided onto grains) [10] are used as well.

2.2 Filling substances/materials

Introduction of filling materials into pores or the deposition on the PS surface is the result of the interaction between the PS and the different technological environments (ion beams, gaseous or liquid). The most frequently used techniques are electrochemical or chemical treatment. Their main advantages are the possibility to deposit materials inside pores, the simplicity of the equipment and the low cost of the process [2]. Other methods such as ion implantation, CVD techniques,

molecular-beam and liquid phase epitaxy, liquid infiltration, spin-on diffusion, and sol-gel techniques are used as well.

Deposit quantity and shape can be varied in wide ranges. It is possible to recognize the following approaches: doping, filling or coating of the internal pore surface, deposition of layer covering the external surface of PS with or without permeation into pores, or formation of composites (Fig. 2).

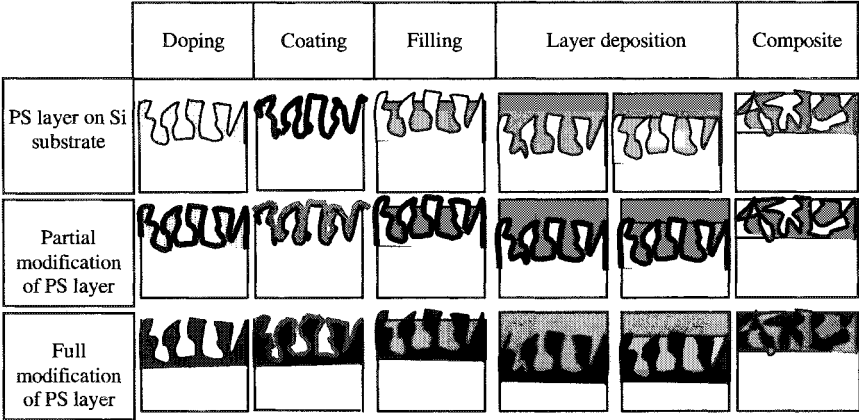


Figure 2. Variants of PS based composite structures.

Rare-earth elements, P, B, Al, O, N, Pd are used for PS doping by ion implantation [5, 11] and spin-on diffusion [12].

Various substances are used to fill or coat the pores: metals (W, In, Ag, Co, Ni, Cu, Zn) [2, 4], semiconductors (CdTe, ZnSe, CdS, SiC) [2, 11], SiO₂ and Si₃N₄ [11], C₆₀ [2], dyes [2], polymers [2, 3], organic liquids [13-15]. Moreover, doped substances or mixtures (Er:Fe [21], Er-doped In₂O₃ [16], Mn-doped Zn₂SiO₄ [17], mixed Sn-V-O oxides [2]) are used as filling materials.

The dimensions of pores and the deposited materials in case of the pores filling have a one to one correspondence, obtaining PS based composite structures with nanosize deposits (e.g., 2-10 nm clusters of W [4] or 20 nm diameter Ni filaments [18]).

Different multi-layered structures are formed using the PS host. These structures consist of upper (sometimes, epitaxial) layer, PS layer with filled or not-filled pores, and single crystal Si substrate.

The monocrystal structure of PS provides the possibility to use it as a buffer layer for heteroepitaxy on Si wafers. Theoretical analysis has shown the existence of optimal PS thickness and porosity range corresponding to minimal heteroepitaxial structure stress [19]. Model result is confirmed experimentally by the positive influence of PS buffer on the structure and properties of diamond, SiC, GaAs [19], PbS, PbTe, InSb, CdTe [1, 2, 19, 20] layers grown on PS.

The PS host based complex contains a mixture of Si nanocrystallites with clusters of filling materials. Formation of Pt-Si composites with grain size of about 100 nm, and polymer-Si composites including the PS grains separated from the Si substrate and mixed with poly(p phenylene-vinylene) are described in [6, 10].

2.3 *Final treatments*

The final treatment is performed with different aims: transformation of the filling materials (diffusion [12], evaporation of a solvent [2, 16], polymerization [3]), the transformation of filling substance-PS system (silicidation [1]), transformation of PS host (partial oxidation [2], complete oxidation [17, 21]).

The oxidation step converts the PS host into SiO₂ and the clusters of the filling material are incorporated into the oxide. The filling materials can keep their chemical composition, i.e. for single filling substance and complete oxidation of PS. The use of a mixture of substances as filling materials allows the formation of clusters with different chemical compositions [21]. In case of partial oxidation the obtained structures also include Si clusters. The oxidation degree controls the size of the Si clusters retained in oxidized PS. As a result, SiO₂ with incorporated nanosize clusters of different composition can be formed.

3 **Application**

The composite structures based on PS have different applications in opto-electronic, optical and microelectronic devices, and in chemical and biomedical technologies. Filling materials, such as rare-earth elements [5, 17, 16, 21], luminescent polymers [10], different dyes [2] define the luminescence wavelength of the PS host based composite structures. Doping or passivation of internal surface of pores [11], filling of pores [2] by metals, conductive polymers, or wide-gap semiconductors improve the characteristics of PS based LED. Infiltration of the pores by other materials provides the modification of wave-guiding properties [13, 14]. Optical media with extremely efficient light scattering (opalescence) [15], with non-linear property [22], particularly, for solitons transfer [23], and photosensitive structures [8, 9] are formed with the use of PS host. Other known applications comprise multilevel metallization for VLSI [4], deep diffusion doping [12], SOI structures [1], heteroepitaxial structures [1, 19, 20], high effective electron emitters [24], sensors [2, 6], magnetic materials [18], heterogeneous metal catalysts [25]; membranes for molecular filters [26], and biomaterials [2, 27].

Considering the PS properties and wide variability of PS based technology, it is reasonable to forecast the extension of PS host application in nanotechnology, and the development of new PS host based composite nanostructures.

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NANOPOROUS ANODIC OXIDE ON ALUMINUM – TITANIUM ALLOYS

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Anodization of Al-Ti alloys with a Ti concentration in the range of 1-35 % has been performed to fabricate a composite nanoporous oxide. An increase of the Ti content is found to enlarge few times the size of pores. Composite oxide films with the weight fraction of the titanium oxide exceeding that of the aluminum oxide have been formed for the first time. The new nanostructured material has properties as alumina (Al_2O_3) as well as titanium oxide.

1 Introduction

Porous anodic alumina attracts an attention of a scientific community due to an ordering nanostructure resulting from self-regulated electrochemical anodic process. Aluminum is a unique material, which forms a regular porous oxide, composed of a packed array of columnar hexagonal cells, each having a cylindrical pore in the center [1]. The cell size is known to be determined by the electrolyte and anodization regimes [1,2]. We have found that the cell size can be also tuned by Ti in Al-Ti alloys. The results obtained are presented in this paper.

2 Experimental

Al-Ti alloy films were fabricated by magnetron sputtering of an Al target composed with Ti insets. An area of Ti insets was from 1 to 40 % of the total sputtering area. The thickness of the films was 0.25-1.2 μm . Electrochemical anodic oxidation was carried out in 10 % aqueous solution H_2SO_4 at forming current densities (J_f) from 3 to 20 mA/cm^2 .

The composition of the as-deposited alloy films and anodized films was determined by Auger spectrometry (PHI-660 Perkin Elmer) after five seconds of ion milling of the films. The oxide films were also analyzed with scanning and transmission electron microscopy (TEM). The refractive index of the oxide was measured at $\lambda = 633 \text{ nm}$ by ellipsometer LEF - 3M.

3 Results and discussion

Fig. 1(a) shows concentration profiles of the components in the as-deposited and anodized film fabricated by magnetron sputtering of the composed target with the 25 % Ti inset area. The average content of Ti atoms in the as-deposited film was 27 %. They were uniformly distributed over the film thickness. Oxygen on top of the film relates to the native oxide. Similar results have been obtained for alloy films with another content of Ti. The difference between percentage of the Ti inset area and concentration of Ti atoms in deposited films was less than 10 %.

It should be noted, that maximum forming voltage (U_f) for an aluminium anodic process in an aqueous sulfuric solution is 30 V [1]. Our investigations have showed that forming voltage for Al-Ti alloys can reach 90-100 V in the same electrolyte. This result is new because the forming voltage determines the size of a cell in the porous oxide [1].

Fig. 1(b) shows Auger profiles of the components in the anodized Al-Ti alloy film. The distribution of Al and Ti atoms are still uniform over the film thickness. Therefore we conclude that pores have uniformly passed through the film. Taking into account the stoichiometric ratio of metal and oxygen atoms in Al_2O_3 and TiO_2 one can calculate that the formed oxide has the deficit of oxygen atoms and the surplus of Ti atoms. The oxygen deficit can be explained by the presence of a non-stoichiometric oxide with oxygen vacancies. Moreover, a fraction of Ti atoms can be in unbound states like it takes place with Si atoms in anodized Al-Si alloys [3]. Currently an actual state of surplus Ti atoms remains unknown.

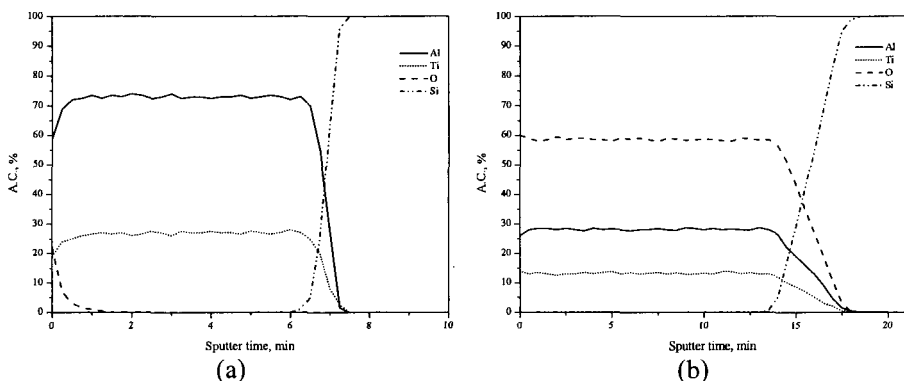


Figure 1. Auger depth profiles of elements in Al-Ti alloy films before (a) and after (b) anodization.

Fig. 2 shows TEM images of the investigated porous oxide films. The top layer is porous oxide of Al-Ti alloy with the content of Al and Ti atoms 73% and 27%, respectively. The bottom layer is pure porous alumina. There are regular porous structures in both cases. However, the size of the hexagonal cells differs considerably.

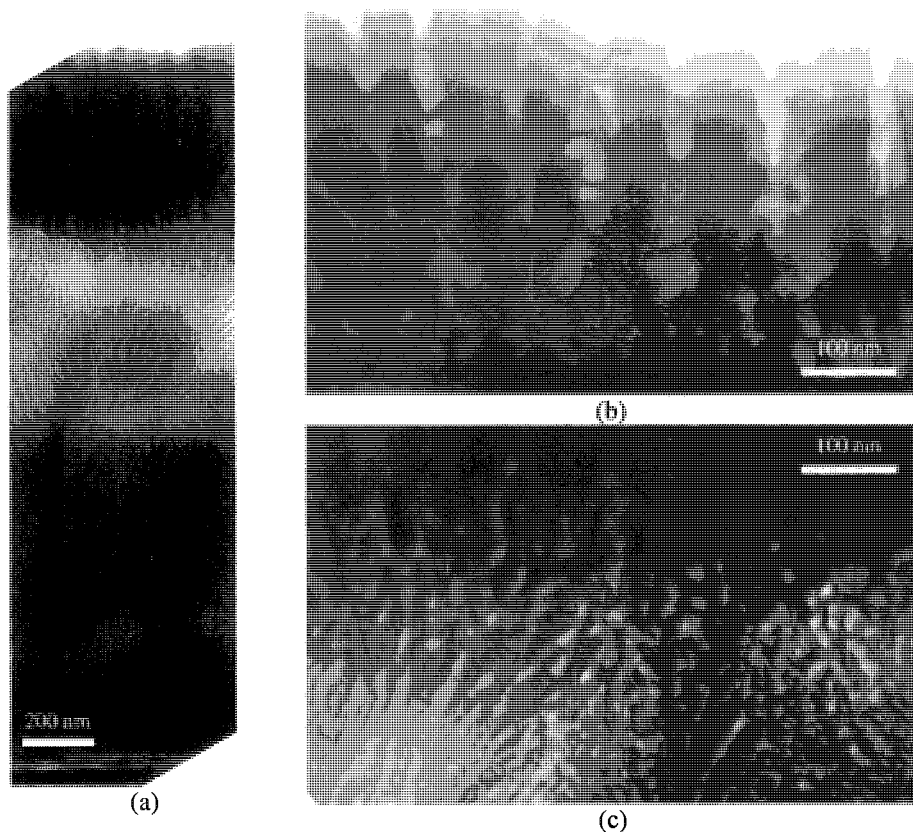


Figure 2. TEM image of porous oxide films: (a) the overall view of the film, (b) the top layer of porous oxide of Al (73 %) – Ti (27 %) alloy film formed at $U_f=35$ V, (c) the bottom layer of porous oxide of pure alumina formed at $U_f=11$ V.

Structure and optical parameters of the porous oxide films are listed in Table 1 for different Ti content. The size of the porous oxide cells is seen to change considerably in comparison with pure alumina films. Dielectric constant and refractive index can be changed gradually with varying of the Ti content in the alloy films.

It should be specially noted that we have managed to form porous oxides on Al-Ti alloys with the content of Ti atoms in the as-deposited films up to 35 %. Taking into account the weigh densities of Al_2O_3 and TiO_2 one can calculate the specific weigh for each oxide. In this case the specific weigh part of TiO_2 was higher than that of Al_2O_3 . It means that we have got the anodic porous oxide film with the regular hexagonal structure where the most weigh part belongs to the

material that is different from Al_2O_3 . According to our knowledge such nanostructured anodic material has been formed for the first time.

Table 1. The parameters of porous oxide films.

Initial film and anodization regimes, U_f, J_f	Pore diameter, nm	Pore wall thickness, nm	Film porosity, %	Volume expansion factor	Refractive index
Al(73 at.%)–Ti(27 at.%), 35 V, 3 mA/cm ²	20–40	40–70	12	1.52	1.74
Al(86 at.%)–Ti(14 at.%), 30 V, 10 mA/cm ²	20–35	35–60	14	1.42	1.62
Al, 11 V, 10 mA/cm ²	9–13	9–19	18	1.35	1.40

4 Conclusion

A new nanoporous material based on anodic Al_2O_3 and TiO_2 has been fabricated by anodization of Al–Ti alloys. The size of pores and pore walls can be tuned by both anodization regimes and Ti content in the alloy. The formed anodic oxide has properties as Al_2O_3 as well as TiO_2 . For example the fabricated oxide films demonstrated a photovoltage generation under UV (3.7 eV) irradiation [4]. This effect is attributed to nanostructured TiO_2 [5]. Moreover the developed technique allows fabrication of the waveguides with the core made of the material with high refractive index [6]. Thus, the fabrication of new nanostructures based on anodic Al_2O_3 and TiO_2 oxides opens new possibilities for nanoelectronics and nanophotonics.

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BIREFRINGENCE AND PHOTONIC BAND GAP IN POROUS ALUMINA FILMS

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Porous anodic alumina films prepared in oxalic and tartaric acids were demonstrated to reveal properties of birefringent or photonic band gap media depending on the pore size and distance.

1 Introduction

Porous anodic alumina (PAA) has a wide application in protection and decorative coating, electrolytic capacitors, host matrix for metal nanowire and carbon nanotube deposition. PAA consists of close packed near hexagonal cells with hollow channel at each cell axis.

A normal orientation of pores allows a large anisotropy of the oxide optical properties. Diameters of the cells varies from tens to hundreds nanometers depending on the electrolyte composition and anodic current density. That opens prospects of applications of PAA in photonics. First, PAA films should have strong form birefringence due to the pore propagation along the normal to surface. Second, the pores of a wavelength size allow to produce two-dimensional photonic crystals [1]. Photonic crystal formation requires a preliminary nanometric ordering of a luminum su rface, e .g., b y n anoimprinting and e lectropolishing, a nd results in fabrication of highly ordered porous structures [2, 3]. On the other hand, formation of nanorelief on Al surface is observed during long-time process of porous alumina production. After selective chemical etching of the oxide the subsequent oxidation at the same regime results in the ordered PAA growth.

In the present work, we employ the latter technique for fabrication of new photonic structures as two-dimensional photonic band-gap (PBG) crystals and layers with strong birefringence in the visible range.

2 Experimental

PAA films were formed by anodization of Al foil of 100 μm thickness in oxalic (40 g/l, sample 1) and tartaric (60 g/l, sample 2) acids at constant current density of 10 mA/cm^2 . According to the measurements in optical microscopy and SEM the thickness and period of structure averaged for the sample 1 were about 42 μm and 100 nm for the sample 2-about 6 μm and 500 nm, respectively. After the oxide formation a non-oxidized aluminum was etched selectively to produce a transparency window for optical measurements. Finally, the samples were rinsed in DI during 10 min and then dried in air at 150 $^{\circ}\text{C}$.

3 Results and discussion

Transmission spectra for the sample 1 in parallel and perpendicular polarizers were measured for different angles of incidence in visible and near infrared ranges. The obtained results indicate an optical axis lying along the pores. At oblique angles the anisotropy increases with increasing angle of incidence (Fig. 1).

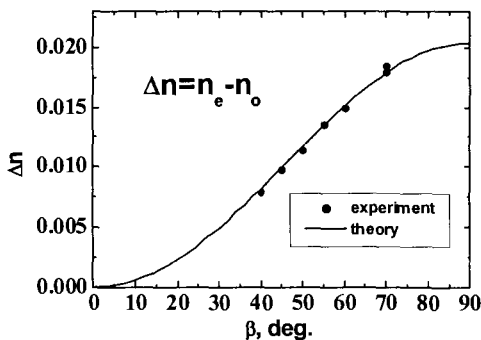


Figure 1. Dependence of the difference between the refractive indices for extraordinary and ordinary waves in the porous alumina (sample 1) on the angle of incidence. The solid line is the fitted dependence for a positive crystal.

The value of birefringence in PAA reaches 0.06 for light propagated in the direction perpendicular to the pore axes. The porosity of sample 1 estimated by modified Bruggeman effective media approximation was about 16%, whereas in compliance with the model [1] it was 18%.

Fig. 2 presents transmission spectra for the light polarized perpendicular to the pores for the sample 2. The transmittance rises with increasing of the angle of incidence, whereas the transmission minimum has a red shift. At normal incidence PBG disappeared. The presence of PBG in the sample 2 at oblique angles indicates to its satisfactory optical quality and highly ordered pore structure.

High optical quality of the PAA membranes allowed us to investigate precisely kinetics of pore widening. The measurements of PAA refractive index variation

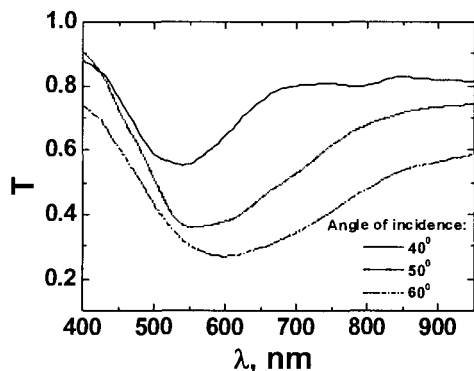


Figure 2. Transmission spectra of porous alumina (sample 2) for different angles of incidence.

during chemical etching of the oxide showed that porosity of the samples may be increased up to 67% without deteriorating of optical properties. This fact shows an additional prospect to varying birefringence and PBG position of PAA-based photonic crystals.

In conclusion, we found that electrochemical oxidization of the aluminum foil at room temperature allow us to fabricate high quality porous alumina films. Depending on the structure the films would be useful for optics either as homogeneous medium with large birefringence or as a photonic crystal. In both cases the optical properties of porous alumina are tunable by varying porosity. Good agreement between calculated and measured structural and optical parameters of PAA makes this material suitable for investigation of PBG properties. Taking into account our recent results in CdS and CdSe electrodeposition into pores of PAA [4] allows us to predict a possibility of new optical phenomena in photonic crystals embedded with semiconductor materials.

Acknowledgements

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ANISOTROPIC LIGHT SCATTERING BY POROUS ANODIC ALUMINA

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We present experimental results on light scattering by porous anodic alumina membranes and show that probability of light scattering has a maximum in the direction along pores.

1 Introduction

In the last decades, porous anodic alumina (PAA) attracts much attention due to its unique self-organized, reproducible morphology [1]. The structure of PAA comprises an array of hexagonal cells of anodic alumina, each containing a cylindrical pore. Fabrication of PAA is realized through electrochemical anodizing of aluminum, generally in inorganic acid solutions. PAA is optically transparent from visible to IR range, possesses high mechanical and thermal durability. By selecting the anodizing conditions, the appropriate geometry (pore diameter, distance between cells, and depth of porous layer) may be obtained. Furthermore, by consideration of the anodizing conditions (e.g. two-step anodizing, pre-texturing of the aluminum surface, etc), highly-ordered, high-aspect ratio porous layers may be promoted [2]. There are proposals of optical applications of PAA in two-dimensional photonic bandgap materials [3]. Other optical applications may be promoted by the effect of the luminescence enhancement from materials embedded into a matrix of PAA via sol-gel process, originating from multiple scattering of exciting light into pore channels and, as a result, increasing the probability of the lanthanide ions to be excited [4].

In this paper, we concern another consequence of the light scattering into PAA membrane resulting in occurrence of spatial anisotropy of emergent light.

2 Experimental

The membranes of PAA were fabricated by anodizing of preliminary polished aluminum foils (99.999 %) in 1.2 M phosphoric acid at the constant current density

of 5.5 mA/cm^2 at $13 \pm 1^\circ\text{C}$. After anodizing, the remaining aluminum substrate was removed in a saturated HgCl_2 solution. The resulting thickness of PAA layer was about $70 \text{ }\mu\text{m}$.

In the experimental setup (Fig. 1) the sample (membrane of PAA) and the detector can turn around the axis passing through the sample plane. Such scheme permits to make experiments on light scattering by a sample at different angles of laser beam incidence as well as experiments on transmission diagrams investigation.

Experiments were performed with two light sources: He-Ne gas laser (632 nm) and solid state Nd-laser pumped with a semiconductor laser (second harmonic, 531 nm). Laser radiation was focused at the sample plane. Cross-section area of the focused beam was $\sim 1 \text{ mm}^2$.

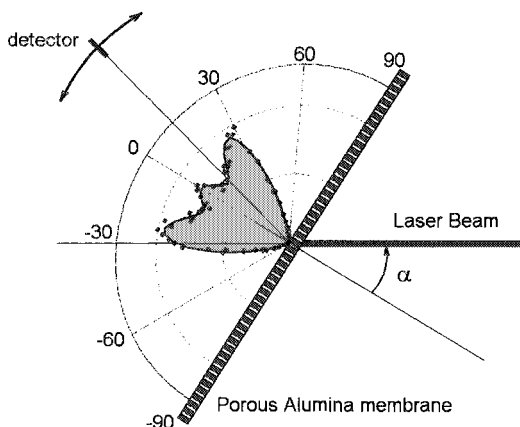


Figure 1. Scheme of the experimental setup.

3 Results and discussion

The structure of the PAA layer before removing from the aluminum substrate (Fig. 2). The structure represents almost parallel pores array with average pore diameter and distance between cells 100 and 300 nm, correspondingly.

Porous alumina membranes have optical transmission up to 97% at normal incidence. This means that such membranes are more transparent than any continuous dielectric material (e.g., glass optical transmission $\sim 93\%$). Shapes of the transmission angular dependencies on angle are different for different wavelengths because pore diameter, distance between the cells and light wavelength have comparable values (Fig. 3a). Scattering indicatrices for different angles of incidence have been measured (Fig. 3b).

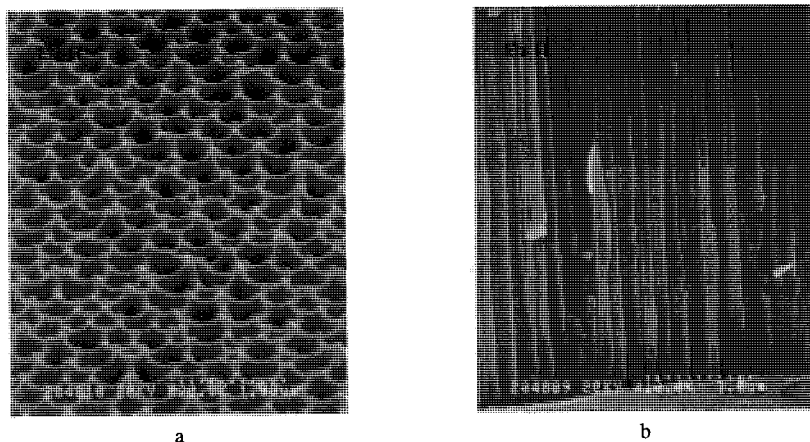


Figure 2. SEM images of the porous anodic alumina: a – top view, b – cross-section view.

There are three peaks on the scattering indicatrices (Fig. 3b): the first is in the initial direction of light propagation, the second is in the “mirror reflection direction”, and the third is in the direction perpendicular to the planar sample surface.

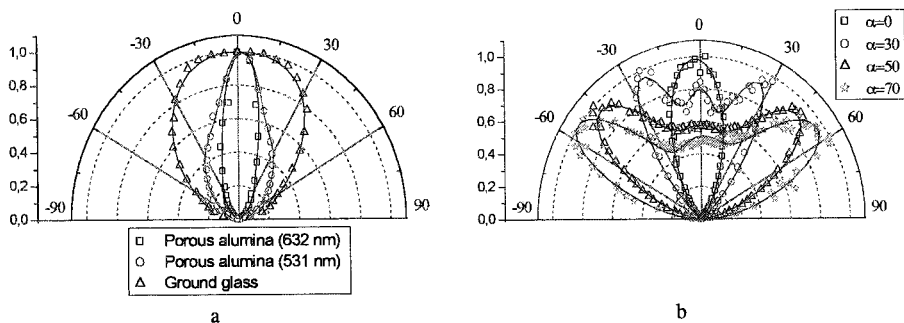


Figure 3. Transmission diagrams of the porous alumina membrane and ground glass for two wavelengths (632 nm and 531 nm) (a). Scattering indicatrices for different angles (α) of laser beam incidence. Wavelength of scattered light is 632 nm (He-Ne laser) (b).

Mechanism of the peak formation is interpreted as follows. The first peak is the light passed through the sample in the initial direction. The second one corresponds to the light reflected by regular parallel pores. The third peak appears because PAA membranes are not perfect (rough pore surfaces, reflection index heterogeneities). Light diffusely scatters on these defects under non-isotropic density of photon states (DOPS) conditions. Probability of light scattering in certain direction is proportional to the DOPS in this direction [5]. DOPS has a maximum value in the direction along pores and a minimum in the perpendicular directions. Therefore, light mainly scatters in the direction along pore axes and the third peak appears.

4 Conclusion

In conclusion, the revealed maximum of light scattering in the direction parallel to pore axis resulting in spatial anisotropy of emergent light is connected with non-isotropic distribution of DOPS. This effect may be utilized in creation of light sources with directed radiation based on PAA membranes.

Acknowledgements

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PHOTOLUMINESCENCE EXCITATION SPECTROSCOPY OF ERBIUM INCORPORATED WITH IRON IN OXIDIZED POROUS SILICON

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Photoluminescence excitation (PLE) spectroscopy was carried out at 77K on oxidized porous silicon containing iron/erbium oxide clusters. The novel PLE spectrum of the 1535 nm Er PL band comprises a broad band extending from 350 to 570 nm and very weak bands located at 640, 840, and 895 nm. The excitation at wavelengths of 400 – 560 nm was shown to be the most effective. No resonant PLE peaks related to the direct optical excitation of Er by absorption of pump photons were observed. The lack of the direct optical excitation indicates conclusively that Er is in the bound state and may be excited by the energy transfer within the clusters.

1 Introduction

Optical properties of dielectrics can be modified by incorporating nanosize clusters of foreign materials. Recently Si nanoclusters were shown to excite rare-earth element Er in the silica glass host [1,2]. The favorable effect of Si nanoclusters on the photoluminescence of Er in oxidized porous silicon (OPS) was also demonstrated [3]. In silica hosts doped with Si nanoclusters it was shown that the excitation energy can be transferred from nanoclusters to Er ions located in a silica-like environment near the clusters. Nowadays, there is a principal interest to incorporate Er ions inside clusters due to influence on the excitation process.

In [4] we demonstrated for the first time that Er ions can be incorporated inside iron oxide clusters of OPS. These 5-50 nm clusters were formed by electrochemical co-deposition of Fe and Er in porous silicon followed by high temperature oxidation. The Er ions incorporated in the iron oxide nanoclusters showed a highly resolved Stark structure of emission spectrum indicating unambiguously a well-defined configuration of Er centers in crystalline environment [4,5]. We have observed more than twenty sharp emission peaks related to highly resolved transitions between splitted spin-orbit levels of the $^4I_{13/2}$ and $^4I_{15/2}$ multiplets. The FWHM of the peaks did not exceed 0.5 meV at 77 K that is much lower than that for Er in different silica-like host materials. Two ensembles of different Er centers having cubic and lower than cubic symmetries have been identified [5].

In this paper, a photoluminescence excitation (PLE) spectroscopy is carried out to reveal the mechanism of luminescence from Er incorporated inside the iron oxide clusters in OPS.

2 Experimental

Uniform 1.5 μm thick PS layers were formed by anodization of p-type Si wafers of 0.3 Ohm cm resistivity in 48% HF. After anodization, the HF electrolyte was replaced by a 0.1M FeSO_4 +0.001M $\text{Er}(\text{NO}_3)_3$ solution and a Fe:Er film was electrochemically deposited into PS. As SIMS analysis showed, both Er and Fe can be introduced deeply into PS by this electrochemical technique [5]. The maximum Er and Fe concentrations were estimated to be 0.1 and 10 at. %. The samples were oxidized at 500°C for 360 min and then at 1100°C for 15 min in O_2 atmosphere. This treatment has been shown to form 5-50 nm iron/erbium oxide clusters inside OPS [5]. As comparison reference, Er-doped OPS containing Si clusters (without Fe) samples were fabricated in a similar way by polarization of PS in an $\text{Er}(\text{NO}_3)_3$ solution. Photoluminescence excitation (PLE) spectra were recorded at 77 K by a grating spectrometer MDR-23 equipped with a Ge:Cu detector. A Xe lamp was used as the excitation source.

3 Results and discussion

The excitation mechanism of Er in OPS was investigated by measuring the intensity of the strongest 1.53 μm PL peak as a function of excitation wavelength. Fig. 1 shows the PLE spectra for two samples: (a) OPS:Si:Er - oxidized PS doped with Er (without Fe) and containing Si clusters, and (b) OPS:Fe:Er:O - oxidized PS containing Fe:Er:O clusters.

PLE spectrum of OPS:Si:Er is an overlay of a broad band (dashed line) and sharp peaks located at 381, 523, 654, and 980 nm. The 300 to 600 nm broad band spectrum is attributed to Er ions excitation process involving Si nanoclusters in the partially oxidized PS host. The sharp peaks indicate direct optical excitation of Er ions incorporated into the oxide phase of OPS [3].

The PLE spectrum of OPS:Fe:Er:O consists of a broad band extending from 350 to 570 nm and very weak bands located at 640, 840, and 895 nm. The excitation at wavelengths of 400 – 560 nm is clearly the most effective. We did not observe any resonant PLE peaks related to the direct optical excitation of Er. The lack of the direct optical excitation of Er is a very important result indicating that Er ions in the OPS:Fe:Er:O are in the bound state and may be excited predominantly by the energy transfer within the clusters. When Er and Fe are electrochemically co-deposited into PS followed by a high-temperature oxidation, they form Fe:Er:O nanoclusters and Er is incorporated inside the clusters. Although the exact structure and chemical composition of the nanoclusters require further investigation, we

believe that the Fe:Er:O clusters are responsible for Er excitation for the wavelength range of 400-560 nm and for weak Er excitation for the 895, 840 and 640 nm. Indeed, it is known that Fe(III) and Fe(II) oxides display wide absorption bands at 11.000-12.000 cm^{-1} , 15.000-18.000 cm^{-1} , and 25.000 cm^{-1} [6]. These absorption bands coincide well with the excitation bands of Er in OPS:Fe:Er:O at 895(11.173 cm^{-1}), 840(11.9040 cm^{-1}), and 640(15.625 cm^{-1}) nm.

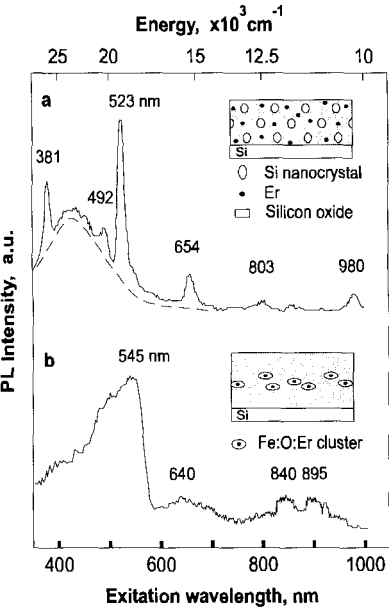


Figure 1. PLE spectra of OPS:Si:Er(a) and OPS:Fe:Er:O(b).

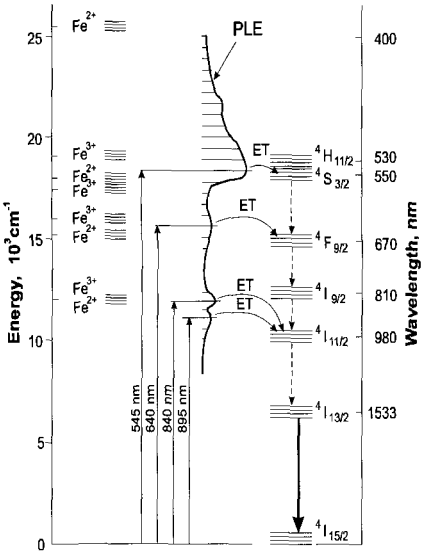


Figure 2. Schematic diagram of the excitation and luminescence of Er in PS:Fe:Er:O.

Fig. 2 shows the energy-level diagram that illustrates the possible excitation and luminescence mechanism of Er^{3+} in OPS:Fe:Er:O. Light from an external source is absorbed by Fe:Er:O clusters in the wavelength range of 350-570 nm and at 895, 840 and 640 nm. The energy of absorbed photons slightly exceeds the corresponding Er^{3+} energy levels, namely, multiplets $^4\text{I}_{11/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$ and $^4\text{H}_{11/2}$. Energy transfer (ET) to Er^{3+} ions inside the clusters is realized by a non-radiative resonance mechanism [7]. The relaxation process takes place towards the metastable $^4\text{I}_{13/2}$ level, from which 1.53 μm light is emitted. Due to the broad absorption bands of iron oxide nanoclusters the excitation scheme would allow optical pumping of Er ions by a broadband light source.

The detailed energy transfer mechanism of Er^{3+} ions inside clusters is required for further fundamental understanding. Gaining deeper insight into the synthesis of Fe:Er:O clusters and excitation mechanism of Er^{3+} ions is a crucial step for the

realization of active optical devices based on OPS doped with Er and different bonding in the form of clusters.

4 Conclusion

We have shown that nanoclusters of Fe:Er:O incorporated in OPS may be responsible for the absorption of exciting radiation and Er excitation occurs through the non-radiative energy transfer of absorbed energy to Er ions inside nanoclusters. The PLE spectrum comprises no resonant features but a broad band range from 350 to 570 nm. In-depth study of the synthesis mechanism of Fe:Er:O clusters and PL mechanism of optically active Er ions inside the clusters provides a way for the design of cluster-sensitized Er doped amplification medium based on OPS. In this medium Er can be pumped efficiently using a broad range of pump wavelengths.

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IMPURITY STATES IN IMPLANTED POROUS ANODIC ALUMINA

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Formation of Ti metal clusters and Cu₂O during Ti or Cu ions implantation into porous anodic alumina was revealed in this work. Electron energies in KVV O and KLL Al transitions in amorphous and γ porous alumina films were determined.

1 Introduction

Porous anodic alumina is a very promising material for nanoelectronics. The injection of different types of impurities inside an alumina matrix can substantially improve its electrophysical properties. It is very important to study the local environment (chemical bonds, electronic structure, etc.) of injected atoms for understanding physical principles of the electronic elements formation. A number of techniques can be used to determine a chemical state of atoms in near surface layers. The most informative and precise technique is X-ray photoelectron spectroscopy. At the same time, Auger electron spectroscopy (AES) is also used for a chemical analysis [1] and can be even applicable for an analysis of dielectrics. The chemical state analysis of Ti and Cu atoms implanted into anodic alumina films was carried out in this work by means of AES.

2 Experimental details

Porous anodic alumina (AA) films were obtained by anodizing aluminum in 5% solution of oxalic acid at 60 V and 13.5°C. Two types of samples with the film thickness of 100 and 200 μm were prepared. After electrochemical processing AA films were amorphous. Their crystalline state ($\gamma\text{-Al}_2\text{O}_3$) was produced by 6 h thermal annealing at 830°C in air.

The implantation of Ti and Cu ions into crystalline AA films from the barrier layer side was carried out using a MEVVA source with pulse duration of 1ms. The applied acceleration voltage was 80 kV, the ion current density was 53 $\mu\text{A}/\text{cm}^2$, the dose was $1.5 \cdot 10^{18}$ ions/ cm^2 . The temperature monitored on the sample holder did not exceed 820°C during the implantation.

The chemical state analysis was carried out by means of AES (PHI-660) combined with Ar ions sputtering at an energy of 3 keV.

3 Results

AES depth profiles of Ti and Cu ions implanted in AA films are presented in Fig. 1. The derivative Auger electron spectra of Ti implanted samples were taken before sputtering and after 3 s of sputtering. No significant changes between them are found. The selected region of the spectra after 3 s of sputtering is shown in Fig. 2.

One can see that the electron energy in the Ti LMV transition is 418.5 ± 0.5 eV. For TiO_2 and TiO compounds the electron energy in the Ti LMV transition is varied in the range of 414.7-414.9 eV [2], while for Ti it is 419 eV [2]. One can conclude that at the surface Ti atoms are mainly found in metal precipitates. A similar Ti atoms state was observed for 0.5-7 keV Ti implantation into sapphire [3]. Also for all incident energies and implantation temperatures studied (RT-750°C) metallic Ti states were predominantly presented only in the near surface region, while increasingly oxidized states (Ti_2O , TiO , TiO_2 , Al_2TiO_5) dominated at the interior of the modified layer [3].

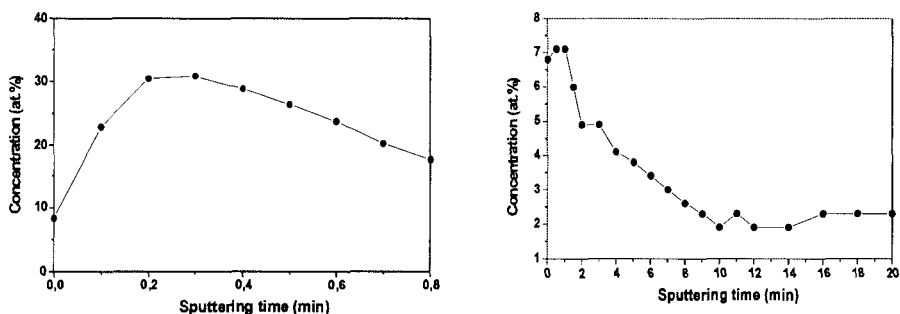


Figure 1. AES depth profiles of Ti (left) and Cu (right) in 200 μm and 100 μm AA samples.

The form of different Auger transitions in the case of Cu implantation is almost independent on sputtering time. Spectra taken before sputtering and after 4 min of sputtering were the same. The Cu LMM transition has two minima: 916.0 ± 0.5 eV and 918.0 ± 0.5 eV (Fig. 2). The energy in the main minimum is close to the electrons energy in the Cu LMM transition for Cu_2O compound, 916.8 eV [4]. For CuO this value is 917.9 eV [2] and for Cu - 918.65 eV [5]. The second minimum can be attributed to metallic Cu or CuO . At the same time, the intensity of the signal is too low to clearly separate different components. One can say definitely on formation of Cu_2O compound. Similar results were observed earlier after 0.75 - 1.5 MeV Cu implantation into sapphire followed by annealing at 1000°C [6].

Implantation of Cu ions into polycrystalline α -alumina results in another phase composition [7]. After 110 keV Cu implantation and 800-1000°C annealing monoclinic CuO and spinel phase CuAl_2O_4 were observed. Moreover, after annealing at 1200°C the whole quantity of copper completely disappeared and the alumina surface did not display any precipitates [7]. In our case strong diffusion of

Cu atoms is also observed (Fig. 1). This fact allows to suppose that the temperature of the samples during implantation was higher than 820°C registered on the samples holder. All these data show that the final phase composition is strongly dependent on implantation regimes and a type of alumina substrate used.

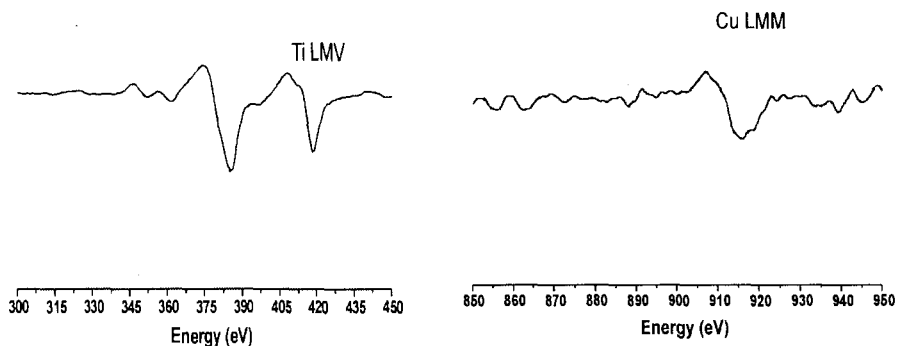


Figure 2. AES derivative line shape of Ti LMV transition in Ti implanted 200 μm AA sample (left) and Cu LMM transition in Cu implanted 100 μm AA sample (right).

KVV O and KLL Al Auger transitions have differences in the case of Ti and Cu ion implantation (Fig. 3). For Ti implantation the electron energy in KVV O and KLL Al is $510.4 \text{ eV} \pm 0.5 \text{ eV}$ and $1390.0 \pm 0.5 \text{ eV}$, respectively. For Cu implantation these values are $505.6 \pm 0.5 \text{ eV}$, $510.4 \pm 0.5 \text{ eV}$ and $1386.0 \pm 0.5 \text{ eV}$. The KLL Al transition is very sensitive to a type of alumina bonds and hydrogen presence in alumina. But literature data in this respect are very contradictory. For example, for $\gamma\text{-Al}_2\text{O}_3$ the KLL Al transition energy varies in the range of 1377–1388 eV [8]. In any case the main reason for these differences could be connected with different crystalline states of alumina after implantation because Ti ions are mainly bound in metallic precipitates, and the concentration of Cu atoms is too low to affect the KVV O transition significantly. Earlier conducted X-ray diffraction investigations showed that implantation of Ti ions resulted in the transformation of a crystalline structure into an amorphous one, while implantation of Cu ions did not change its structure. Electron energies of $510.4 \text{ eV} \pm 0.5 \text{ eV}$ in KVV O and $1390.0 \pm 0.5 \text{ eV}$ in KLL Al transitions can be attributed to amorphous AA film, and electron energies of $505.6 \text{ eV} \pm 0.5 \text{ eV}$ in KVV O and $1386.0 \pm 0.5 \text{ eV}$ in KLL Al transitions can be due to γ AA film.

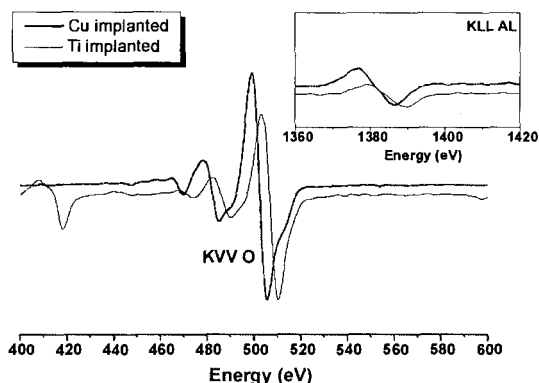


Figure 3. AES derivative line shape of KVV O and KLL Al transitions in Ti and Cu implanted AA samples.

4 Conclusion

The implantation of Ti and Cu ions into porous AA films resulted in the formation of metal Ti and Cu_2O precipitates in the near surface region. These agree with the data on Ti and Cu implantation into sapphire accompanied by postimplantation annealing.

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EVIDENCE FOR ENERGY TRANSFER BETWEEN Eu^{3+} AND Tb^{3+} IN POROUS SILICON MATRIX

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Terbium and europium have been incorporated into luminescent porous silicon (PS) by impregnation of PS layers in chloride solution of rare earth. The concentration dependencies of photoluminescence (PL) intensity are examined and Rutherford Back-scattering Spectrometry (RBS) measurements are performed. The excitation mechanisms of Eu^{3+} and Tb^{3+} ions in the PS matrix are discussed.

1 Introduction

Due to the strong absorption of the ligands in the ultraviolet region and efficient energy transfer from the ligands to the central rare earth ions, lanthanide organic coordinate compounds usually exhibit good luminescence characteristics, such as high color purity and high efficiency. To make these materials applicable for technological uses the complexes must be incorporated into a rigid matrix possessing good optical properties as well as high thermal and chemical stability. Some of rare earth complexes have been incorporated into PS matrix by different methods, and the resulting composites possess good thermal stability and mechanical properties [1,2]. When compared with other techniques, the impregnation method [3-8] presents some advantages such as the possibility of depositing on complex shapes, an easy control of the doping level, rather inexpensive starting materials and simple equipment.

In this work, we present the optical properties of Eu^{3+} in PS (Eu^{3+}/PS) nanocomposites. The effect of co-doping with Eu^{3+} and Tb^{3+} ($\text{Eu}^{3+}+\text{Tb}^{3+}/\text{PS}$) is also studied.

2 Experimental

PS samples were prepared by electrochemical anodization of p-type Si (100) wafers with resistivity of 0.7-1.4 $\Omega \text{ cm}$. The electrolyte used for anodization was a HF solution (40%), ethanol and H_2O ($\text{HF}/\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}=2:1:1$ in volume). The anodization current density and the etching time were 12 mA/cm^2 and 3 min,

respectively. After etching, the samples were rinsed with dionized water and dried in air at room temperature. The porosity of PS layers is about 70% and the thickness is less than 2 μm .

PS layers have been impregnated in chloride solution of europium for more than 2 hours to ensure total infiltration of Eu^{3+} . Just after the infiltration, the sample was dried by nitrogen gas. In a second step, the PS layer was impregnated in a mixture of EuCl_3 :ethanol and TbCl_3 :ethanol solutions to form $(\text{Eu}^{3+}+\text{Tb}^{3+})/\text{PS}$ nanocomposites. Three parts of the same PS sample impregnated in the same conditions. We have used three different concentrations of $(\text{EuCl}_3+\text{TbCl}_3)$: ethanol solution (C, 2C and 4C).

Emission spectra were measured by exciting the samples with an argon laser. The luminescence signal was analyzed with a triple monochromator and detected with a GaAs photomultiplier. All measurements were performed at room temperature. The samples composition and penetration were investigated with the RBS method by using 2 MeV $^4\text{He}^+$ ions.

The TEM thin foils were prepared from the film on the substrate following the conventional cross section method. Cross section TEM observation were observed using a high resolution electron microscope TOPCON 002B.

3 Results and discussion

Fig. 1 displays the RBS spectra of the PS layer (a) and Eu^{3+}/PS after subsequent annealing at 1000°C for 60 s. The spectrum (b) reveals the penetration of europium in the PS layer. The Eu^{3+} signal presents a plateau (1050-1734 keV) in higher energy position which indicates clearly a complete penetration of this specie over most of the PS layer.

Fig. 2 shows the PL spectra before (a), after impregnation in EuCl_3 solution (b) and after annealing at 1000°C for 60 s (c). The excitation wavelength is 465.8 nm corresponding to the high luminescence from Eu^{3+} [7] which corresponds to the energy of $^5\text{D}_2 \rightarrow ^7\text{F}_0$ transition. Untreated PS has a broad PL spectrum peaked at $\approx 14340\text{ cm}^{-1}$. After impregnation, we note the presence of several peaks. These peaks were identified as the characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_j$ (where $j = 0,1,2,3,4$) transition of Eu^{3+} ions, which indicate that Eu^{3+} ions are present in the PS. Thermal treatment is in our case used to stabilize the rare earth-related luminescence. The Eu^{3+}/PS nanocomposite annealed at 1000°C in air exhibit strong emission of Eu^{3+} ions (Fig. 1c). The PL peaks of Eu^{3+} become efficient and resolved. It is a sign for

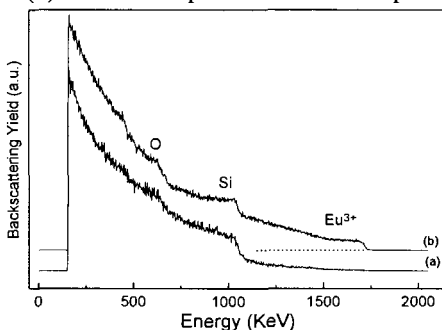


Figure 1. RBS spectra of PS layer (a) and Eu^{3+}/PS nanocomposite after annealing at 1000°C (b).

optical activation of the sites. It seems that Eu^{3+} ions are diffused in PS (Si crystallites) at this temperature.

After impregnation, the PL band of PS does not quenched which can indicate that excitation transfer from Si nanocrystallites to Eu^{3+} ions is not possible. Furthermore, in a previous work [7], we have shown that Eu^{3+} emission in PS depends strongly on laser excitation which exclude the process of radiative excitation transfer from PS to Eu^{3+} .

The cross section TEM of the Eu^{3+} /PS sample annealed at 1000°C is shown in Fig. 3. The top of the image consists of Eu^{3+} /PS region. The very dark region represents the silicon substrate. The total thickness of PS doped Eu^{3+} is in this case about 330 nm. The presence of Eu^{3+} ions inside PS has been checked from EDX spectrum recorded along the cross section of the sample. The diagram shows the presence of two peaks associated to Eu whose positions appear at higher energy. We note also the presence of higher intensity peaks associated to the O ($\approx 66.3\%$) and Si ($\approx 32.5\%$) atoms.

The Eu^{3+} ions percentages in a PS matrix is about of 1.2%. This percentage is approximately equal over the whole PS thickness (three measurements are taken: in the top, middle and the base of Eu^{3+} /PS region), indicating a complete and uniform penetration of Eu^{3+} over most of the PS layer. Conclusions from EDX observations have been confirmed by RBS analysis.

To improve the energy excitation transfer from rare earth to Si nanocrystallites, we have studied the effect of co-doping of the PS layer with Eu^{3+} and Tb^{3+} in equal proportion. Fig. 4 displays the RBS spectra of PS samples after europium and terbium deposition and subsequent annealing. Due to the close atomic numbers of terbium and europium and to the overlapping of their respective isotopic

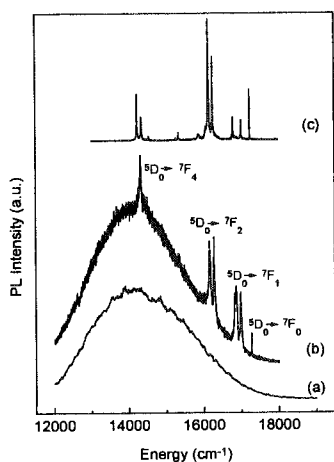


Figure 2. PL spectra of PS layer (a), Eu^{3+} /PS nanocomposite (b) and after annealing at 1000°C (c).

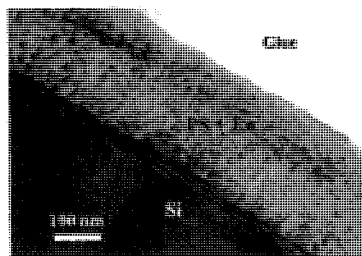


Figure 3. Cross section TEM image of the Eu^{3+} /PS nanocomposites after annealing at 1000°C for 60 s.

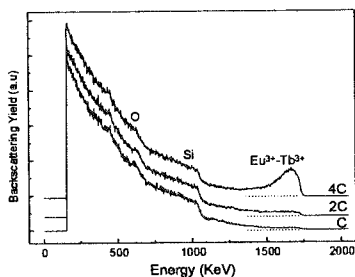


Figure 4. Dependence of RBS spectra on Eu^{3+} - Tb^{3+} concentration. (Eu^{3+} + Tb^{3+})/PS nanocomposites are annealing at 700°C for 60 s.

masses distributions, it is impossible to discriminate the Tb^{3+} signal from Eu^{3+} signal. The separated peaks in the spectrum and the large band at the high energy side indicate clearly a total and uniform penetration of Tb^{3+} and Eu^{3+} into the PS layer.

The integrated peak's areas are not equal for the three different concentrations. However, an increase of the $Eu^{3+} - Tb^{3+}$ signal is observed, when the concentration of the solution increases. This can be only related to the presence of more rare earth ions, when the sample is impregnated with more concentrated solution. The following estimation for the corresponding concentration of $Eu^{3+} - Tb^{3+}$ ions over Si ratios can be given: 1.1%, 1.6% and 2.4% respectively when the concentration of the solution increases.

The PL spectra for $\lambda_{exc}=488$ nm of $(Eu^{3+}+Tb^{3+})/PS$ nanocomposite are shown in Fig. 5a. By increasing the concentration of $Eu^{3+}-Tb^{3+}$ solution, we show an increase of the PL intensity for Eu^{3+} and Tb^{3+} emission. Moreover, we confirm the RBS results in Fig. 4. It was found also, that the PL intensity of PS emission increases when the concentration of the solution increases. Nevertheless, the Eu^{3+} ions in PS are directly excited by absorption of laser energy. The same result has been shown with Tb^{3+} ions in PS [6,8]. Each behavior suggests that energy transfer can occur from rare earth (Eu^{3+} and Tb^{3+}) ions to Si nanocrystallites.

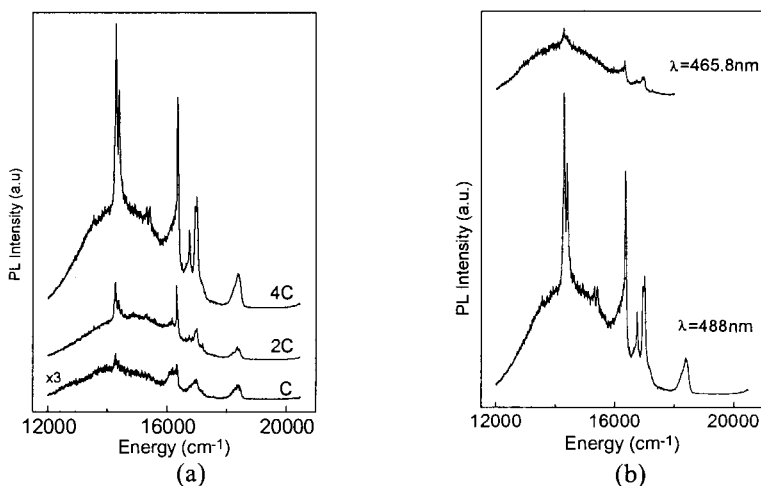


Figure 5. (a). PL dependence on $(Eu^{3+}+Tb^{3+})$ concentration. The excitation line is 488 nm. (b). Comparison between the PL spectra of $(Eu^{3+}+Tb^{3+})/PS$ excited by the 488nm and 465.8 nm rays.

This suggestion is proved by comparing for the same sample, the PL signals of $(Eu^{3+}-Tb^{3+})/PS$ corresponding to 465.8 nm and 488 nm (Fig. 5b). The peaks related to Tb^{3+} appear only for the last ray and the peaks of Eu^{3+} become more efficient compared to those excited with the 465.8 nm ray. The fact that the optimized PL of Eu^{3+} in PS appears for the 488 nm ray and not for 465.8 nm [7] is an indication of

the contribution of other process to the emission. Three different processes of excitation transfer can occur: from Tb^{3+} to Eu^{3+} , from Tb^{3+} to Si nanocrystallites and from Eu^{3+} to Si nanocrystallites. There are two channels of energy transfer in Eu^{3+} - Tb^{3+} PL. One is non-radiative resonant transfer from Tb^{3+} to Eu^{3+} ions. The other is radiative resonant transfer, i.e., absorption by Eu^{3+} ions of photon emitted by Tb^{3+} ions.

4 Conclusion

We have developed PS doped Eu^{3+} or Tb^{3+} and Eu^{3+} by a simple impregnation method. RBS and EDX/TEM analysis reveal a complete penetration of rare earth (Eu^{3+} and Tb^{3+}) in the nanometric pores of PS. The PL study shows that Eu^{3+} are diffused in Si nanocrystallites and occupies crystallographic sites in the matrix after annealing at 1000°C. We show that the luminescence of (Eu^{3+} + Tb^{3+})/PS depends directly on wavelength excitation, which suggests that a process of excitation transfer occurs from Tb^{3+} to Eu^{3+} and to Si nanocrystallites when the radiative resonant transfer does play a key role.

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ELECTROLUMINESCENT XEROGELS FABRICATED IN POROUS ANODIC ALUMINA

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For the first time, the electroluminescent structures based on sol-gel derived SnO_2 and In_2O_3 films containing 30 wt.% Eu_2O_3 and Tb_2O_3 are fabricated onto porous anodic alumina. The current-voltage characteristics and the dependence of emission intensity on annealing temperature are considered.

1 Introduction

Electroluminescent (EL) devices are currently the focus of substantial research efforts due to potential application in flat panel displays. The most of the works in this area is directed to synthesis of organic EL materials, and high luminous efficiencies at low operational voltages have been demonstrated [1]. However, organic compounds generally have a number of disadvantages, including poor thermal and mechanical stability. In addition, while electrical transport in organic materials has improved, the room temperature mobility is fundamentally limited by the weak van der Waals interactions between organic molecules (as opposed to the stronger covalent and ionic forces in extended inorganic systems) [2]. Therefore, the stability and electrical transport characteristics of organic materials contribute to reduced device lifetime. The most widespread inorganic sulfide-based phosphors such as ZnS:Mn , SrS:Cu etc, in contrast, have inappropriate voltage-current characteristic with the threshold voltage above 150 V below which little light is emitted [3]. Further, such materials have wide emission bands, and their synthesis involves expensive vacuum processes.

In this connection, it is of interest to use oxide-based phosphor materials that may be synthesized via simpler methods, such as chemical deposition [4], sol-gel synthesis [5], and offer excellent chemical and thermal stability. By embedding the

trivalent lanthanide ions into such materials during the synthesis process, the emission in the visible spectral range is achieved. Furthermore, the lanthanide ions have narrow and fixed spectral bands and theoretical upper limit of quantum efficiency is about 100% that is unachievable for other materials.

Our recent investigations demonstrated that sol-gel films doped with lanthanides allows strong enhancement of photoluminescence (PL) when fabricated in porous anodic alumina (PAA) [6]. In the present paper, we report on investigations of Eu- and Tb-doped In_2O_3 and SnO_2 sol-gel-derived films fabricated in PAA in view of an application in EL devices.

2 Experimental

The samples of PAA were fabricated by anodizing of aluminum layer deposited by magnetron sputtering onto silicon substrates. The anodizing was carried out in 1.2 M H_3PO_4 at constant current density of 5.5 mA/cm^2 . In_2O_3 and SnO_2 sols containing Tb_2O_3 or Eu_2O_3 were deposited onto PAA by spinning at 2700 rpm for 30 s. Then, annealing in air for 20 min was performed in the temperature range 200–900 °C.

To investigate the EL features of the structures, an ITO electrode formed onto glass surface was mechanically pressed onto top surface of PAA filled with xerogels (Fig. 1 a), the silicon substrate served as the second electrode. PL measurements were performed using Ar^+ ion cw laser operating at $\lambda=300 \text{ nm}$ for excitation.

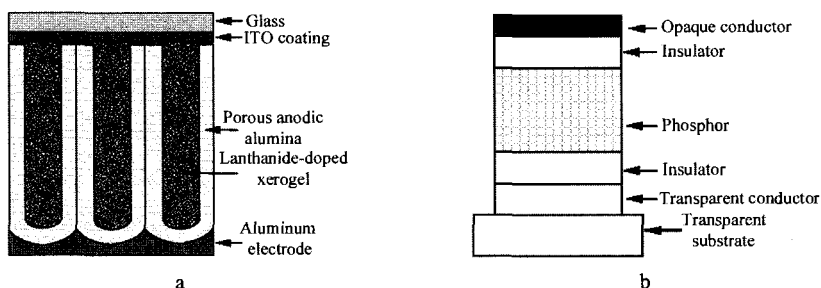


Figure 1. Schematic views of EL cells: a – based on PAA- lanthanide-doped xerogels; b – standard type.

3 Results and discussion

The standard EL device (Fig. 1 b) employs a transparent substrate, typically glass, coated with a transparent conducting layer, which serves as the bottom electrode. The bottom insulator, phosphor, and top insulator layers reside between the bottom transparent conductor and a top opaque conducting layer. This layer serves both as an electrical contact and as a reflector to direct light generated in the phosphor layer

out through the glass substrate. The purpose of insulating layers is limitation of the current flowing through the phosphor, and prevention of the breakdown between two electrodes due to possible inhomogeneity of the thin phosphor layer.

The second design of EL device is so-called inverted structure. It is similar to the standard structure and contains the same insulator-phosphor-insulator sandwich, but the inverted structure is built on an opaque substrate. A transparent top contact is employed. The inverted structure makes it possible to use higher processing temperatures than the standard structure, since a substrate with a melting point higher than that of glass can be used. Another variant of the EL device structure is the single insulator structure. In this structure, the top insulator is not deposited in order to simplify processing.

The following advantages are achieved utilizing PAA as a template of EL cell:

- the simpler fabrication (the cell structure is formed during anodization: insulator layer is the barrier layer of PAA, the template for phosphor is the porous layer, the one of the electrode is the non-anodized aluminum or silicon substrate),
- inhomogeneity of phosphor layer does not degrade the performance of device (porous layer prevents the breakdown between two electrodes, therewith by choosing its thickness the high breakdown voltage may be achieved),
- both PAA and xerogel films allows high-temperature processing.

The voltage-current characteristics (VCC) of the EL structures are presented in Fig. 2. In_2O_3 xerogel based structures operate at lower voltages than that of SnO_2 . The visible emission in red (Eu-doped xerogels) and green (Tb) regions appears at the voltages above 40 and 90 V for In_2O_3 and SnO_2 xerogels, respectively, when the positive potential is applied to the ITO electrode. From the shape of VCC it could be concluded that the EL mechanism involves a double injection (holes from the ITO layer and electrons from the bottom electrode) and recombination of carriers in the phosphor with transferring the energy to lanthanide ions resulting in a photon emission. Both the samples with PAA thickness of 5 and 15 μm demonstrated visually about equal intensity of emission.

To investigate the temperature stability of the structures, the PL measurements were carried out in relation to Eu-doped xerogels formed on PAA and monocrystalline Si substrates and annealed in the range of 200–900°C (Fig. 3). It was difficult to perform correctly the analogous EL measurements, because the mechanical ITO contact did not provide the necessary accuracy. PAA changes the PL behavior with a annealing temperature in comparison to flat substrate. The minimum in intensity appears near 500°C. As a whole, the PL intensity changes weakly for In_2O_3 xerogel with the processing temperature, whereas as for SnO_2 xerogels the higher temperatures are more appropriate that could be connected with crystallization processes at high temperatures [5].

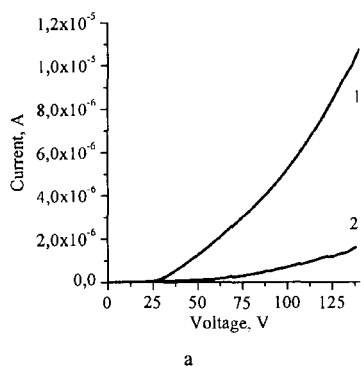


Figure 2. Voltage-current characteristics of EL structure fabricated on PAA of 15 μm thick: xerogel $\text{Eu}_2\text{O}_3\text{-In}_2\text{O}_3$ (curve 1), $\text{Eu}_2\text{O}_3\text{-SnO}_2$ (curve 2). Sample dimensions are $5 \times 5 \text{ mm}^2$.

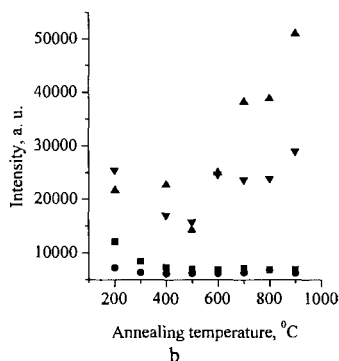


Figure 3. PL intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ spectral band (612 nm) from Eu_2O_3 in In_2O_3 xerogel fabricated on mono-Si ($\bullet$), SnO_2 on mono-Si ($\blacksquare$), In_2O_3 on PAA of 5 μm thick ($\blacktriangledown$), and SnO_2 on PAA ($\blacktriangle$).

4 Conclusion

The EL structures based on lanthanide-doped inorganic xerogel and PAA were studied for the first time. In spite of high operating voltages, the structures are of great interest due to absence of organic compounds and possibility to manipulate the design and performance of the device by tailoring PAA morphology. Further efforts on increasing stability and performance will be done with replacement of mechanical ITO contact with the same sol-gel derived film and modification of xerogels toward lowering operating voltages by increasing electrical conductivity.

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PERIODIC NANOSTRUCTURES FABRICATED BY ANODIC OXIDATION OF VALVE METAL FILMS

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Electrochemical anodization of multi-layer Al/Ta/Al thin film compositions was developed to fabricate regular nanostructures of tantalum oxide (Ta_2O_5). Anodization kinetics, space characteristics of Ta_2O_5 nanopillars and electrical properties of Al/ Ta_2O_5 /Al structures have been studied. Al/Ta/Al thin film compositions were shown to permit formation of regular nanostructured layers appropriate for photonic crystal and nanoelectronic applications.

1 Introduction

Periodic nanostructured layers promise wide applications in electronic and optoelectronic devices. Photoelectrochemical and electrochromic structures are among them [1]. The most suitable process for formation of such layers is electrochemical anodization of tantalum-aluminum multi-layer thin-film compositions. This process is inexpensive and permits to form nanostructured pillar layers of Ta_2O_5 with large surface area. Details of Ta_2O_5 pillar formation from two-layer Al/Ta thin film compositions were described in our previous papers [2,3]. The main purpose of our further investigations was to investigate the processes of anodization of a multi-layer Al/Ta/Al structure. It was found that application of the bottom Al layer improves uniformity of nanostructured pillar layers due to more homogeneous current supply. Besides, this layer serves as an electrode of a metal/dielectric/metal (MDM) structure. Furthermore, such metals as Nb and Ti may be used instead of Ta layer.

In this paper, we present a method of fabrication of periodic nanostructured layers in the thin film system Al/Ta/Al. Main kinetic features of the anodization process and properties of the nanostructures formed have been studied.

2 Experimental

Ta films, Al/Ta and Al/Ta/Al thin film structures were deposited onto dielectric substrates using electron beam evaporation technique. The bottom Al layer was deposited to provide an electric contact to the intermediate Ta layer during its anodic oxidation and to form more uniform structure. Upper and bottom Al layers were then also used for electrical characterization of the structures formed by the

anodization. Al films thickness was 1 μm (for bottom layer) and 0.7 μm (for upper layer). Ta film thickness was 0.07 or 0.15 μm . The anodization was performed in potentiostatic and galvanostatic regimes at room temperature. Main characteristics of the anodization process are listed in Table 1. Different electrolytes have been tested to select the best one.

Table 1. Experimental characteristics of Al/Ta structure anodization.

N	Thickness of Ta in Al/Ta structures	Electrolyte	Concentration, %	pH	V_{max} , V	J_a , mA/cm^2	k_a , nm/V	C, nF/cm^2
1	0.15 μm	Ammonium pentaborate in ethylene-glycol	17	6	250	3-5	1.0	70
2	0.15 μm	Citric acid aqueous solution	1	2	250	1.5-2.0	1.7	65
3	0.15 μm	Orthophosphoric acid aqueous solution	4	1	200	3-5	1.25	60
4	0.15 μm	Oxalic acid aqueous solution	4	0	180	3-5	1.4	50
1	0.07 μm	Ammonium pentaborate in ethylene-glycol	17	6	250	3-3.5	1.2	
2	0.07 μm	Citric acid aqueous solution	1	2	250	1.5-2.0	1.2	
3	0.07 μm	Orthophosphoric acid aqueous solution	4	1	150	2.5-3.0	1.2	
4	0.07 μm	Oxalic acid aqueous solution	4	0	140	2,0-3,5	1.2	

Capacitance of the anodic Ta_2O_5 films was measured on test MDM structures (Al/ Ta_2O_5 /Al). Upper electrode was deposited through metal mask with diameter of holes 1 and 0.5 mm. Surface structure was analyzed with an atomic force microscope (AFM).

It should be noted that the anodization constant k_a for multi-layer compositions differs from that for a single tantalum film. This is because the anodization voltage for the Ta film on a dielectric substrate is 1.5 to 2 times higher than that in the case of Al bottom layer. Relationships between current density, anodization duration and forming voltage at a constant scanning rate of voltage have been obtained.

3 Results and discussion

Figs. 1,2 show dependencies of J_a vs V_a for Al/Ta and Ta structures in various electrolytes. The anodization current density for investigated compositions differs approximately in 3-4 times. The transition from Ta layer to Al layer is fixed more clearly in electrolytes 1 and 3 (Table 1) by sharp decrease of the anodization current, which was shown previously [2,3] to be caused by the change of the resistivity at the system transition from one metal to another.

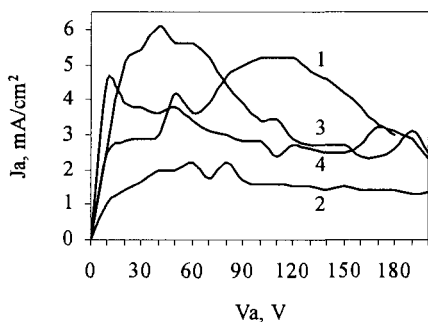


Figure 1. Anodization current density vs anodization voltage for the Al/Ta (0.15 μm) thin film structure being anodized in different electrolytes: the curves indication corresponds to the electrolytes number in the Table 1.

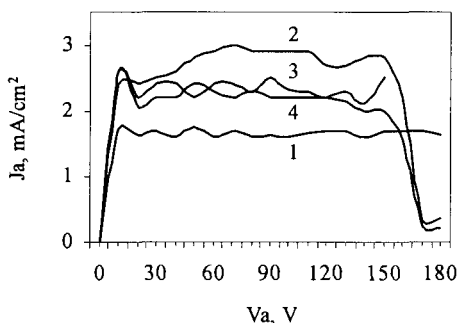


Figure 2. Anodization current density vs anodization voltage for the Ta (0.15 μm) film being anodized in different electrolytes: the curves indication corresponds to the electrolytes number in the Table 1.

Because during anodization of the two-layer structure the cations order changes (the kinetic dependencies character indicates that), only the capacitance value and dielectric losses were measured on experimental MDM structures with upper electrode deposited through mask. Capacitance of the anodic Ta_2O_5 films is 50 to 70 nF/cm^2 . The highest capacitance was obtained after anodization in the electrolyte based on ammonium pentaborate. The dielectric losses value depends on the thickness of remaining aluminum film under the anodic oxide. At the forming voltage less than 150 V, the dielectric losses were in the range of 0.02 - 0.05, but at the forming voltage higher than 150 V they depend on the electrolyte type being in the range of 0.05 - 0.1.

In Fig. 3 the views of the surface of Ta_2O_5 fabricated in various electrolytes and then coated with vacuum deposited nickel layer are shown. It is seen that the surface has a uniform periodic structure, especially in Fig. 3b. In Fig. 3a, the Ni nanodots are seen on the surface of pillars. In Fig. 3b, the whole surface of Ta_2O_5 is covered by the Ni layer. The average pillars diameter was from 6 to 20 nm.

It is known [1] that when electromagnetic radiation with wavelength, comparable to the array's periodicity passes through such an array, the dispersion relation is modified according to the array geometry and composition. Thus, such artificially engineered periodic structures can be used as a photonic crystal.

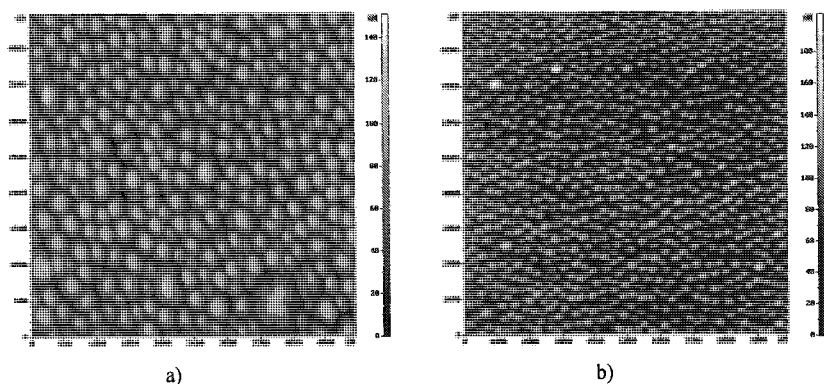


Figure 3. AFM image of surface structured layers of anodic Al-Ta oxides formed in electrolytes based on phosphoric (a) and sulfuric (b) acid and coated with a Ni layer.

In conclusion, it was confirmed that anodization process for multi-layer Al/Ta/Al thin film structure differs considerably from that for two-layer composition. The developed technique permits to produce regular nanostructured layers of various compositions. Formation of nanostructured layers based on anodic Ta, Ti, Nb and Al oxides using multistep anodic oxidation and simultaneous control of their geometrical characteristics will permit to create functional layers for specific applications, in particular for photonic crystals, photoelectrochemical cells, electrochromic displays.

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OPTICAL SPECTROSCOPY OF POROUS COMPOSITES WITH Si NANOCRYSTALS

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We developed an approach for analysis of reflectance spectra with bands of interference origin, for thin porous nanostructured layers on silicon wafers and made the automatic reflectometry equipment to examine optical characteristics (reflectance coefficient, refractive index) in the visible, near- infrared and mid- infrared range. The method is applied to por-Si, por-CoSi₂ and por-Al₂O₃ layers on c-Si substrate. The reflectance spectra, recorded at different light incidence angles permit to detect both the refractive index and layer thickness simultaneously. TEM, AFM, IR spectroscopy investigations of these layers confirmed the presence of Si nanocrystals.

1 Introduction

The principal aim of nanotechnology is creation of novel nanomaterials consisted of metal and semiconductor nanoparticles. Such systems possess new electronic and optical features. We have developed the automatic reflectometry equipment and the method of the simultaneous detection of optical characteristics of thin nanostructured layers.

2 The determination of optical characteristics of thin nanostructured layer

Mirror reflectance spectra from the thin layer on the substrate were measured with different angles of light incidence α_1 and α_2 , corresponding to interference maxima and minima. If the light reflects from the porous layer surface, intensities $I_{max}(\lambda)$ and $I_{min}(\lambda)$ are significantly influenced by the scattering on microinhomogeneities on the front, opposite surfaces and in the bulk of the porous layer [1].

It is possible to obtain values of refractive index n and thickness of layer d from $I_{max}(\lambda)$ (or/and $I_{min}(\lambda)$). The condition for $I_{max}(\lambda)$ reflectivity positions in the reflectance spectra is

$$2d(n^2 - \sin^2 \alpha)^{1/2} = m\lambda, \quad (n > n_{\text{substrate}}), \quad (1)$$

where $m=1, 2, 3, \dots$ For $m=\text{constant}$ (as well as $d=\text{constant}$) we can obtain

$$(n^2 - \sin^2 \alpha_1)^{1/2} / (n^2 - \sin^2 \alpha_2)^{1/2} = \lambda_1 / \lambda_2. \quad (2)$$

From (2) we can obtain

$$n = \{[\sin^2 \alpha_1 - (\lambda_1 / \lambda_2)^2 \sin^2 \alpha_2] / [1 - (\lambda_1 / \lambda_2)^2]\}^{1/2}, \quad (3)$$

where λ_1, λ_2 are the wavelengths corresponded to the same number of maximum with angles of incidence α_1 and α_2 , respectively. If the incidence angle is constant, then we analyze the situation of neighbors maxima in the spectrum. It follows from (2)

$$(m+1)\lambda_2 = m\lambda_1, \quad \lambda_2 < \lambda_1, \quad m = \lambda_2/(\lambda_1 - \lambda_2); \quad d = m\lambda_1/2(n^2 - \sin^2\alpha_1)^{1/2}, \quad (4)$$

where m is the number of interference maximum in the $R(\lambda)$ spectrum corresponding to the wavelength λ .

3 Experimental

The multilayer structures based on CoSi_2 film on por-Si were prepared on p-Si (100) with $\rho \approx 0.006 \text{ Ohm}\cdot\text{cm}$. Por-Si layer is obtained by anodization [2]. Co layer with the thickness of 6.5 nm was deposited onto por-Si surface by electron beam evaporation of Co in vacuum of $7 \cdot 10^{-9}$ Torr. The annealing was performed at 650°C . Standard samples were prepared by etching of c-Si and layer of por- CoSi_2 /layer of Si nanocrystals/por-Si (with different thickness)/c-Si structures. Por-Si layer/c-Si structures are formed after CoSi_2 chemical etching.

Porous Al_2O_3 on c-Si substrate was formed on p-Si ($\rho = 10 \text{ Ohm}\cdot\text{cm}$) substrate by magnetron sputtering of Al layer (0.5 μm) Al and annealing.

4 Results and discussion

The reflectance spectra in the wide range of wavenumbers from 400 cm^{-1} to 30000 cm^{-1} at the angle of light incidence of 20° for the structures under study are given in Fig. 1. The spectra have the following common features: (i) the interference maxima and minima: their position is described using (2)-(4); (ii) the amplitude of waves, reflected both from the front and opposite surfaces of por-Si layer is damped at the increasing of wavenumber.

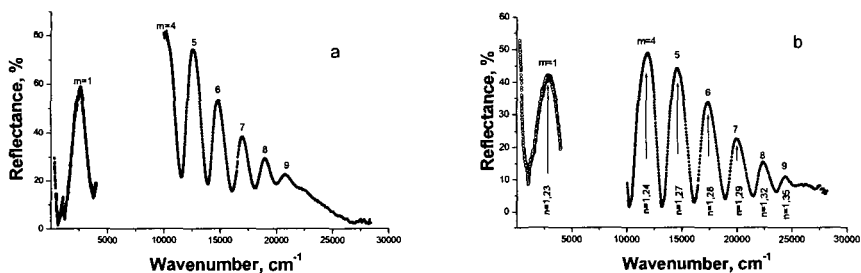


Figure 1. The IR and visible spectra for por- CoSi_2 /layer of Si nanocrystals/por-Si/c-Si structure (a) and layer of Si nanocrystals/por-Si/c-Si structure (b). The structure (b) is formed after chemical etching of por- CoSi_2 . The incidence angle is 20° .

The magnitude of the oscillations is strongly decreased in the range of $10000 - 25000 \text{ cm}^{-1}$. It can be explained by decreasing both reflectivity from the front and opposite surfaces. This indicates that light scattering on roughness of the front and opposite surfaces (por-Si – bulk Si interface) and scattering in the layer are essential.

To verify the roughness role in light scattering for structures with and without por-CoSi₂ layer we compare the dependence of $\ln I_{\max}$ versus λ^{-2} . The line slope in this scale is proportional to roughness parameters in Davies-Bennett relation [3] and the slopes of the plots are the same. So, one can make the conclusion that the roughness parameters for both types of structures are the same. It means that namely the roughness at the por-Si/c-Si interface plays the key role in the light scattering both for por-CoSi₂/por-Si/c-Si and por-Si/c-Si structure.

The reflectance spectra for por-CoSi₂/layer of Si nanocrystals/por-Si/c-Si structure, when the incidence light angle changes from 10° to 45° is presented in Fig. 2. Using these data and expressions (3) and (4), one can calculate the thickness of nanostructured layer and effective refractive index: $d = 1.29 \pm 0.08$, $n_{\text{eff}} = 1.4 - 1.51$ (in the range of $300 - 2500 \text{ cm}^{-1}$), respectively. For the structures without por-CoSi₂ layer it was calculated $d = 1.0 \pm 0.1 \text{ nm}$, $n_{\text{eff}} = 1.23 - 1.35$ (the range of $300 - 2500 \text{ cm}^{-1}$). The estimation of porosity [4] in the last case gives 80%.

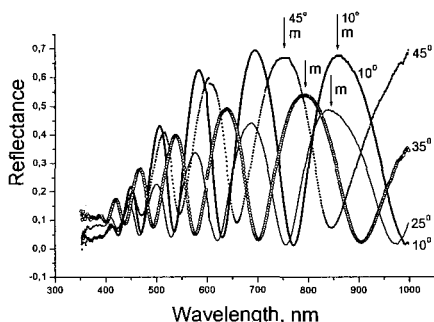


Figure 2. The reflectance spectra for por-CoSi₂/por-Si/c-Si structure, when the incidence light angle varies in the range of 10° , 25° , 35° and 45° . As the example the shift of the point m is shown.

The optical mirror reflectance spectra of the por-Al₂O₃/Si nanocrystals/SiO_x layer on c-Si, recorded at different light incident angles, consist of quasi harmonic oscillations of the reflectance response for any angle (Fig. 3). The magnitude of the oscillations is approximately constant in the range of $350 - 1100 \text{ nm}$. It means that the amplitudes of two reflected beams (from the front and opposite surfaces of por-Al₂O₃/Si nanocrystals/SiO_x layer) are approximately constant in this wavelength range. It can be explained as constant reflectivity from the front and opposite surfaces in the layer. This indicates that scattering on roughness of the front and opposite surfaces and scattering in the layer are negligible in this wavelength range. The refractive index and thickness of the por-Al₂O₃/Si nanocrystals/SiO_x layer calculated using equations (3) and (4) are $n = 1.85 \pm 0.07$, $d = 740 \pm 20 \text{ nm}$, respectively.

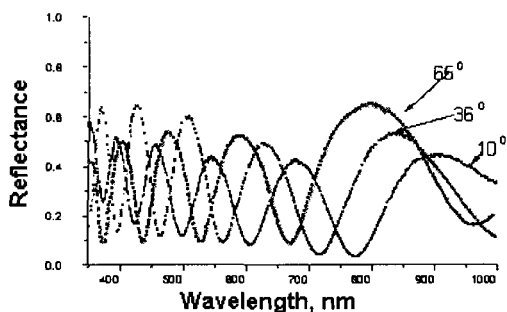


Figure 3. The reflectance spectra at different light incidence angles for the por- $\text{Al}_2\text{O}_3/\text{Si}$ nanocrystals/ SiO_x on c-Si.

To prove the presence of Si nanocrystals in porous composites we analysed their IR spectra. The analysis of IR spectra of the por- $\text{Al}_2\text{O}_3/\text{c-Si}$ structure shows that the most strong and broad absorption band is observed in the range of $578\text{--}614\text{ cm}^{-1}$. It can be assigned to Si-Si vibration modes in nano-Si [5]. The broadening of the band, peaked at 614 cm^{-1} in comparison with c-Si confirms this fact. The absorption at $461, 484\text{ cm}^{-1}$ as well as at $563\text{--}565\text{ cm}^{-1}$ is caused by Si-Si mode absorption in nanocrystals. The strong absorption bands at 728 cm^{-1} and $1063\text{--}1145\text{ cm}^{-1}$ are associated with Si-O-Si (Si-O) stretching. The absorption band at $1095\text{--}1100\text{ cm}^{-1}$ is broadened for Al_2O_3 with Si nanocrystals layer. For it the absorption is additionally observed at 1063 cm^{-1} .

The absorption at 514 and 1015 cm^{-1} corresponds to Al-O, Al-O-Si bonds, respectively. Thus, IR spectra confirm the formation of $\text{Al}_2\text{O}_3/\text{Si}$ nanocrystals/ SiO_x layer on c-Si.

Relief height and the lateral size of “threads” defined from AFM images for por- $\text{Al}_2\text{O}_3/\text{Si}$ nanocrystals/ SiO_x surface are $8\text{--}10$ and $20\text{--}35\text{ nm}$, respectively.

Acknowledgements

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MAGNETIC PROPERTIES OF NANOPARTICLES FORMED IN SOL-GEL FILMS BY ION IRRADIATION OR THERMAL PROCESSING

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Ion irradiation of gel films prepared from mixtures of triethoxysilane with Fe and Ni nitrates permits to obtain a precipitation of metallic particles in a glassy matrix, because of the reduction ability of the hydrido group of the precursor for Fe^{3+} and Ni^{2+} ions. The metal particles, with a narrow range of sizes, exhibit a superparamagnetic behavior in a static field of low amplitude. However, their testing by electron spin resonance put into evidence a correlation of the spins parallel to the film surface.

1 Introduction

Sol-gel chemistry is a useful technique for producing nanomaterials made of particles in an insulating matrix with interesting magnetic or optical properties. Magnetic ordering in such a system depends not only on the formed phases and particles volume fraction, but is also particularly sensitive to the size distribution and spatial dispersion of the particles. In the case of nanocomposites derived from gels, these structural parameters and the material porosity, which are correlated, are determined by the rates of hydrolysis and condensation of the gel precursor (which is generally an alkoxide) and of other reactions of oxidation-reduction occurring during the gelling stage and the subsequent heat treatment. Even though magnetic films are so useful for the storage of information, studies have been performed until now essentially on monoliths and powders obtained by sol-gel chemistry. Beside that, one of the authors demonstrated that ion irradiation is a more suitable means than thermal treatments for converting gels and inorganic polymers into ceramics free of cracks, with a low residual content of hydrogen and a high density [1,2]. Among the various gels which have been submitted to ion irradiation, the one derived from triethoxysilane (TH) is an attractive matrix for its reduction ability of metallic salts. Indeed, the hydrido group of the precursor $\text{SiH}(\text{OC}_2\text{H}_5)_3$ induces the formation of a suboxide $\text{SiO}_{1.5}$ and silicon clusters during conversion treatments. The structure and magnetic properties of TH films containing Fe or Ni after irradiation or heat treatments are studied with the purpose of evidencing the interest

of the TH matrix with respect to TEOS (tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$) and of irradiation for optimizing the dispersion of the magnetic phase.

2 Experimental

The conditions of TH and TEOS hydrolysis and films deposition can be found in [3]. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with a molar ratio of 10% nitrate per alkoxide was added to the gelling solution. Some films, with a thickness of 500 nm, were irradiated with 10^{15} Au ions/cm² of energy 3 MeV stopping into the substrate. This fluence was chosen because the irradiation effects on the gel densification and on the growth of other metallic clusters (Ag, Cu) in both matrices [4]. Other films and monoliths were annealed for 1h at 600 or 1000°C in a vacuum of 10^{-6} Torr.

The structure of samples was studied by X-ray diffraction, at grazing incidence in the case of films, and a few of them were observed by TEM. Two techniques were essentially used for investigating the magnetic properties: electron spin resonance (ESR), with a Brücker spectrometer operating at 9.8 GHz, and direct measurements of their magnetization, with a SQUID magnetometer S600X from Cryogenic Ltd. The two techniques provide complementary information about the magnetic response at low and high frequency of solicitation. Magnetization measurements under low applied field (with a SQUID) as a function of the temperature T are particularly useful for characterizing the behavior of ensembles of small particles. The procedure consisting in recording magnetization curves after zero field cooling (ZFC) and after cooling under low applied field (FC) permits, when the sample is constituted of non-interacting particles, to determine their blocking temperature T_b , related to the energy barrier needed to tilt the magnetic moments [5,6]. Mössbauer spectrometry was also used in the case of annealed monoliths containing Fe, in order to determine the nature and proportion of magnetic phases.

3 Results and discussion

The phases identified by means of XRD, electron diffraction and Mössbauer spectrometry are summarized in Table 1. Irradiated films appear amorphous in XRD, but the broad features observed in the diagrams are centered at the same angles than the mean peaks of α -Fe and Ni in samples containing larger crystallites. Moreover, the precipitation of Fe, Ni particles with mean diameters and standard deviations of 4 ± 1 nm (Ni) and 4 ± 2.5 nm (Fe) is clearly evidenced by means of TEM (Fig. 1). A broader distribution of sizes ranging from 5 to 20 nm is observed in a TH:Ni film annealed at 1000°C (the mean radius found from a set of 500 particles was smaller than the standard deviation). In addition, images of the annealed film show that the matrix is very porous. Annealed samples containing Fe have not yet been observed.

Table 1. Formed phases (main phases are underlined, n.e. is for not examined).

Material	Irradiated film	Film annealed at 600°C	Film annealed at 1000°C	Monolith 600°C	Monolith 1000°C
TH:Fe	α -Fe or Fe_3Si	α -Fe or Fe_3Si	<u>Fe_3Si</u> + Fe_2Si	20% α -Fe + 80% FeSiO_3	20% α -Fe + 80% Fe_2SiO_4
TH:Ni	Ni	Ni	<u>Ni</u> + Ni_3Si + Ni_3Si_2 + Ni_2Si	Ni	Ni
TEOS:Fe	n.e.	n.e.	α - Fe_2O_3	γ - Fe_2O_3	α - Fe_2O_3
TEOS:Ni	n.e.	NiO	NiO	NiO	NiO

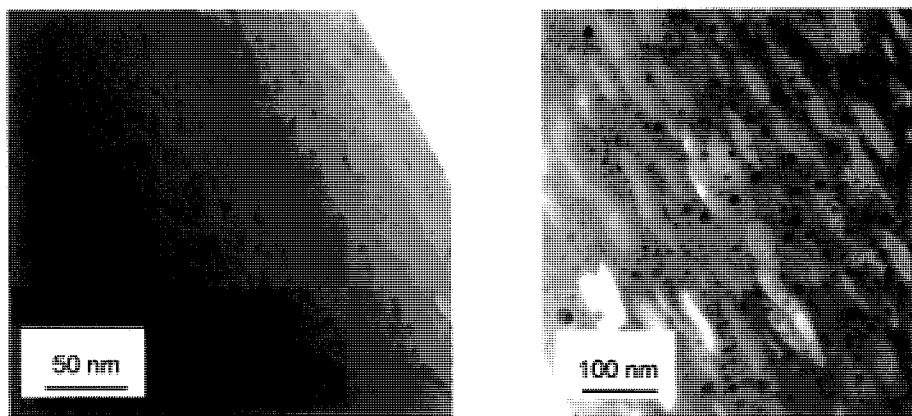


Figure 1. Cross-sections of TH:Ni films irradiated with 10^{15} Au ions (left), annealed at 1000°C (right).

No ferromagnetic resonance is recorded from irradiated TEOS:Ni or TEOS:Fe samples. The spectra of irradiated TH films (on soda-lime substrates) exhibit a sharp peak at 3490-3495 Oe, ascribed to E' centers in the glassy matrix and substrate. A broad and asymmetrical resonance of ferromagnetic atoms overlays that of defects as shown in Fig. 2. The resonance position H_{res} (field at which the derivative of the absorbed energy dI/dH , recorded by modulating the cavity frequency, becomes equal to zero) shifts towards lower values when the applied static field H is perpendicular to the film surface. This anisotropy is commonly observed in thin films, because of the strength of their shape anisotropy factor. Nevertheless, the Kittel's equation [7] for a ferromagnetic plate with homogeneous magnetization does not apply to these films nor to annealed ones, taking into account the non-monotonous variations of the demagnetization field which are obtained. The resonance field H_{res} varies little when H is applied parallel to the surface and it decreases linearly with T in the perpendicular direction. We conclude

from these results that the correlation between magnetic moments is strong parallel to the surface but they exhibit a significant canting. The magnitude of the magnetization M , given by a double integration of the recorded curve, is very comparable in the irradiated films and in the films of the same nature and thickness annealed at 1000°C. It is about 5 times larger for Fe particles than for Ni ones. Rough estimates of the saturation magnetization M_s have been deduced from H_{res} values in the perpendicular direction, of 600 emu for Fe particles and of 1800 emu for Ni ones at room temperature in the irradiated films, as against 1700 and 485 for bulk metals, respectively. Using formula based on the Stoner-Wohlfarth model [6] for the simple case where H is perpendicular to M , anisotropy factors K of 2.5×10^4 erg/cm³ for Fe particles (5×10^{15} in bulk Fe) and 10^5 erg/cm³ for Ni ones (5×10^{14} in bulk Ni) were also deduced from the slopes of the $H_{res}(T)$ lines. The discrepancy between values of M_s and K in particles and in bulk metals could be due to the density of defects in the particles and to their rough interface (in the case of Fe) and to the crude hypothesis made in their calculations that all the metal atoms contained in the films are in the particles (case of Ni).

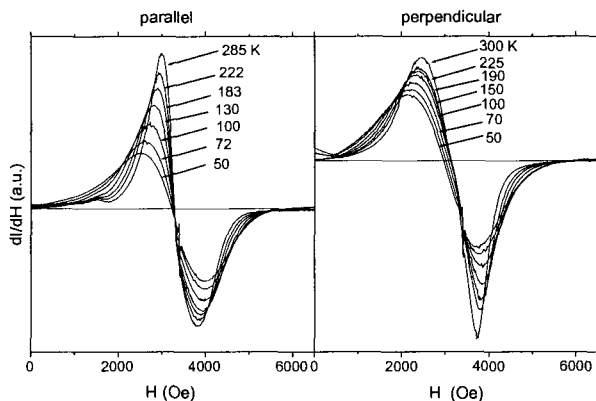


Figure 2. FMR spectra from a TH:Fe film irradiated with 10^{15} Au ions at different temperatures and for 2 orientations of the film with respect to the applied field.

The variations of magnetization, measured with a SQUID magnetometer under a low field of 50 Oe, as a function of T , displayed in Fig. 3 for a film of TH:Fe irradiated with Au ions are typical of superparamagnetic particles. The FC and ZFC curves obey a Curie law in the T range from 50 to 300 K and the ZFC magnetization tends to zero at low T , because moments remain blocked after cooling at 5 K when applying thereafter a field of low amplitude. The magnetization curve $M(H)$ at 5 K is the mixed response of ferromagnetic particles and of paramagnetic defects in the glassy matrix, with a low coercivity of 50 Oe. Using Stoner-Wohlfarth formula [6, 8] relating the anisotropy energy barrier U to the tilt frequency ω of the particles during the time of the experiment t (typically $\omega \sim 10^8 - 10^{10}$ and $t = 10^2$ s) and assuming that these particles have the same M_s and K factor than bulk Fe, one can deduce from the value of the blocking temperature (position of the maximum in the ZFC curve) that the superparamagnetic particles

have a mean radius of 4 nm. This size is significantly larger than the mean value found in TEM, probably because the largest particles, which remain blocked up to higher T, contribute more to the paramagnetic response (in proportion to their number multiplied by the square of their volume). A smaller size, of 1.5 nm, is found from the expression of the Curie constant. Respectively, the blocking temperatures in TH:Fe or TH:Ni samples annealed at 600°C are of the order of 15 to 20 K and the calculated sizes of 3 nm (Fe) and 7 nm (Ni), or of 1-2 nm from the Curie constants. Samples annealed at 1000°C exhibit a ferromagnetic behavior ($M = M_0[1 - kT^{3/2}]$) over the whole range of T, while part of the particles are made of ferrimagnetic (Fe_2Si , Ni_2Si) or paramagnetic silicides (Table 1).

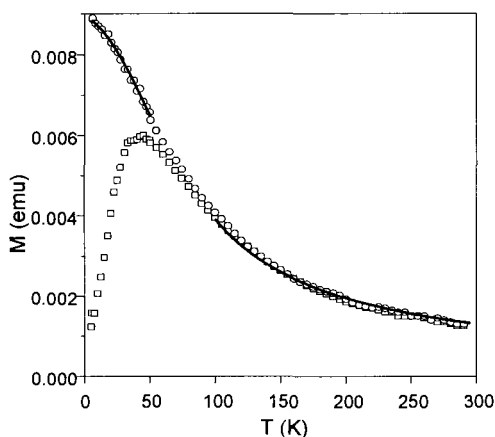


Figure 3. ZFC (squares) and FC (circles) magnetization curves of a TH:Fe sample containing 3 at% (10 mol% FeNO_3) irradiated with 10^{15} Au ions/cm² of 4.5 MeV under a field of 50 Oe. Fits with a Bloch law of ferromagnetism at low T and a Curie law of paramagnetism at high T are shown with a continuous line.

A detailed discussion of the obtained values of Curie constants and shapes of ZFC curves taking into account histograms of cluster sizes, radiation defects, the more or less spherical shape of clusters and their mixed nature (which can be distinguished with a higher magnification in the annealed film of Fig. 1), and so on, would require more experiments. One cannot expect that the magnetic response of a system containing several magnetic phases is simple. The studied $\text{SiO}_{1.5}\text{Fe/Ni}$ composites exhibit for instance an imperfect ferromagnetic correlation in ESR and a superparamagnetic behavior (at high T) in magnetization measurements lasting a longer time. The formation of disordered magnetic phases, like the pyroxene in TH:Fe monoliths annealed at 600°C, put into evidence by Mössbauer spectrometry, is not detected in XRD and gives rise to a weak signal in other magnetic measurements. Thus, it alters the calculation of M_s or of particle sizes based on the hypothesis that all Fe is contained in metallic particles. The core/shell structure observed for some of the Ni/silicide particles in annealed TH:Ni samples, affects most probably the magnetic ordering. If they are imperfectly crystallized, metal particles formed in irradiated films are more interesting for applications because of their uniform nature and size and of their better encapsulation in the matrix.

4 Conclusion

The use of several techniques testing the magnetic response of particles ensembles on different time scales is desirable, especially when their size reaches the limit of resolution in TEM and their diffraction peaks are too broad for permitting the identification of all formed phases. The incorporation of Fe, Ni salts in TH permits to obtain metallic particles by ion irradiation or annealing at low temperatures, simply in vacuum, while undesired phases are formed in TEOS (often even when heat treated in pure H₂ atmosphere [9]). The formation of smaller particles, perfectly encapsulated in dense films of glass, under ion irradiation should permit to increase the areal density of information in magnetic memories.

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DEPOSITION OF NANOPARTICLES ON A COLD SUBSTRATE FROM A LAMINAR GAS FLOW

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Deposition of nanoparticles was investigated in the free molecular regime approximation for thermophoretic force and the Brownian motion. The analytical solution was obtained by the Galerkin method for the heat transfer between gas flow and substrates and convective diffusion. Relative roles of two channels of nanoparticle deposition are discussed.

1 Introduction

The deposition of nanoparticles is an important aspect of a nanostructures creation on a substrate [1,2]. A better understanding of complex interaction in gas dynamic processes, heat transfer and Brownian diffusion is important for proper control of the deposition. In this paper we investigate steady-state deposition of nanoparticles from a laminar flow of a hot gas between two cold flat substrates. We will use a two-dimensional description of all processes in the model.

2 Model

Let axis x to run along the substrates, and axis y to be perpendicular to the substrates as it is shown in Fig. 1. For laminar flow we use the Poiseuille formula [3] for the velocity profile $v(x,y)$ between the substrates $v(x,y)=1.5 u[1-(2y/H)^2]$, where u is the average velocity of gas flow, H is the distance between the substrates.

For description of heat transfer process between hot gas and cold substrates we use the equation:

$$v(x,y)\partial_x T(x,y) = \frac{1}{\rho(x,y)c} \partial_y [\lambda(T(x,y)) \partial_y T(x,y)], \quad (1)$$

where $\rho(x,y)$, c , and $\lambda(T(x,y))$ are, correspondingly, gas density, heat capacity, and heat conductivity. The boundary conditions are $T(0,y)=T_0$; $T(x,H/2)=T(x,-H/2)=T_1$.

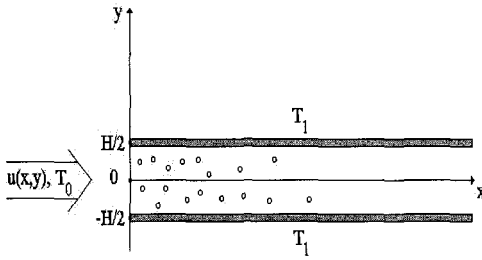


Figure 1. A gas flow and substrates.

For the density of nanoparticles $n(x,y)$ we have the equation of convective Brownian diffusion:

$$v(x,y)\partial_x n(x,y) + v_{th}(x,y)\partial_y n(x,y) = \partial_y D_b \partial_y n(x,y), \quad (2)$$

where D_b is the Brownian diffusion coefficient that is inverse proportional to the squared radius of a nanoparticle in the free-molecular regime, v_{th} is the velocity of nanoparticles induced by the thermophoretic force. It does not depend on radius of a nanoparticle in the free-molecular regime. Note that we neglect thermophoretic effect and Brownian diffusion along gas flow. For our case [4]: $v_{th} = -K\partial_y T(x,y)$ for $y > 0$. Boundary conditions for Eq.(2) can be written as $n(x, H/2) = n(x, -H/2) = 0$, $n(0,y) = n_0$.

For understanding complex interactions between different physical processes affecting nanoparticles, it is very useful to make semi-quantitative estimations [5] by the Galerkin method [6].

3 Semiquantitative estimations

We seek the solution of Eqs. (1,2) in the form $T(x,y) = T_1 + A(x)\cos(\pi y/H)$ and $n(x,y) = B(x)\cos(\pi y/H)$. For approximation of thermophysical parameters, following the standard Galerkin procedure, the functions $A(x)$ and $B(x)$ can be found as a result of the solution of corresponding system of ordinary differential equations. In particular, the temperature profile can be written as:

$$T(x,y) = T_1 + a(T_0 - T_1)\exp\left[-\frac{2\pi^2\lambda}{3H^2u\rho c}x\right]\cos(\pi y/H), \quad (3)$$

where a is the notation for the expression:

$$a = 0.5 \int_{-1}^1 \cos(\pi z/2) dz = 0.636.$$

As it follows from (3), the characteristic length l_t for the temperature relaxation is

$$l_t = \frac{3H^2u\rho c}{2\pi^2\lambda}.$$

Emphasize that for the higher modes, obtained by the Galerkin method, characteristic lengths are much shorter. In turn, if there is no significant temperature gradient, we can neglect the influence of thermophoretic force on deposition of nanoparticles.

The solution of (2) gives the formula for the density of nanoparticles between substrates.

$$n(x, y) = n_0 \cos(\pi y / H) \exp \left\{ -\frac{2\pi^2}{3H^2 ub} [D_b x - K(T_0 - T_1) c l_t (\exp(-x / l_t) - 1)] \right\}, \quad (4)$$

where $b = 0.5 \int_{-1}^1 \cos^2(\pi z / 2) dz = 0.8693$, $c_1 = 0.5 \int_{-1}^1 \cos(\pi z / 2) \sin^2(\pi z / 2) dz = 0.424$.

The characteristic length for the Brownian deposition is $l_b = 3H^2 bu / 2\pi^2 D_b$. It depends on the nanoparticle radius R . To remind that in the free molecular regime $D_b = 3kT / 32\sqrt{2}P\pi R^2 < c >$, where P is the gas pressure, $< c > = (8kT / \pi m)^{0.5}$ is the mean thermal velocity of gas molecules with mass m , k is the Boltzman constant.

4 Discussion

The flux of deposited nanoparticles at the distance x $F(x)$ is

$$F(x) = \int_{-H/2}^{H/2} [n_0 - n(x, y)] v(x, y) dy.$$

This integral can be calculated by using results of numerical simulation or our semi-quantitative estimations, which permit to make parametric studies very effectively. In fact, the thermophysical coefficients of gas flow are temperature dependent. For detailed comparison of theoretical and experimental results, a numerical simulation is also desired.

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COMMENSURATE LONG-PERIOD NANOSTRUCTURES IN ALLOYS

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On the basis of *ab initio* calculations of the electronic structure and electronic susceptibility, the relations between the nesting properties of the Fermi surface and the features of commensurate long-period nanostructures in alloys have been studied.

1 Introduction and computational details

Ordered alloys with a long-period structure are one of the most interesting and promising classes of metal alloys. They differ from ordinary ordered systems with a simple superstructure in the periodic or quasi-periodic disruption of the ordered arrangement of atoms by antiphase boundaries (APB). These periods have nanoscale lengths. Antiphase boundaries are usually energetically unfavorable in ordered alloys but they are equilibrium structural elements in systems with a long-period state. Distinct regions of stability exist on the temperature-composition phase diagrams of alloys with a long-period nanostructure (LPNS) [1].

Studies of mechanical properties of alloys of this type [2-4] have shown that it is possible, by means of ageing, to obtain highly dispersed stable alloys based on

long-period ordered phases. Strengthening of the alloy by the decomposition of a supersaturated solid solution can be effectively combined with strengthening from atomic ordering which in turn makes it possible to create unusual dispersed decomposition structures that are stable. Alloys formed on this basis have high mechanical properties and are stable throughout the temperature range in which the matrix remains ordered [5-6].

According to their type LPNS can be divided into two groups – commensurate and incommensurate. The latter LPNSs occur in CuAu, Cu₃Au, Au₃Cu, Cu₃Pd, and Cu₃Pt. They are characterized by a random spacing M between APB (antiphase domains of varying length are stochastically spread along [001]). The half-period M averaged over a random ensemble varies continuously with composition assuming, among others, irrational values. A common feature of incommensurate states is the fact that they are stable only in the temperature range bounded above by a symmetrical (disordered) phase and below – by a short-period ordered structure. In our early works the electronic nature of formation and stability of the incommensurate LPNS and also two-dimensional structures in Au₃Cu and Cu₃Pd was explained [1,7,8].

Commensurate LPNS are found in Ag₃Mg and Al₃Ti alloys. They represent a strictly regular (ordered) mixture of antiphase domains of varying length such that the average period $2M$ is invariably expressed as a rational fraction m/n (where m and n are integers). When the alloy composition is varied, the value of m/n changes in a discrete manner, and one observes a so-called “devil’s staircase” of commensurate transitions considered along the axis of concentration. As the temperature is varied, m/n changes discretely or remains constant. Similar to incommensurate LPNS, commensurate structures precipitate from a disordered solution as a result of first order phase transition. However, unlike incommensurate structures, the latter remains stable as the temperature decreases, without undergoing any transformation.

In this paper we calculate the electron energy spectra by the full-potential LMTO method within the local electron density approximation [9] to explain the features of commensurate LPNS. The exchange-correlation potential was taken from [10], and the integration over the occupied states was performed using the tetrahedron method [11], with 165 (Ag₃Mg) and 126 (Al₃Ti) reference points used in calculating the spectrum $\varepsilon_k(\mathbf{k})$ and 1771 points in irreducible part of the Brillouin zone in calculating $\chi(\mathbf{q})$. The lattice parameter was taken to be 7.766 a.u. and 7.264 a.u. for Ag₃Mg and Al₃Ti, respectively. When calculating the susceptibility $\chi(\mathbf{q})$ we included only those energy bands that intersected the Fermi level and determined the behavior of this parameter.

2 Results and discussion

In Fig. 1 the susceptibility $\chi(\mathbf{q})$ of the Ag₃Mg alloy ordered as $L1_2$ is shown. It was calculated along the Γ -X direction of the Brillouin zone (Γ -X corresponding to the

$\langle 100 \rangle$ direction along which the LPNS is formed). It exhibits a sharp maximum at the wave vector $\mathbf{q} = (2\pi/a)[0.284, 0, 0]$ which points to the instability of the hypothetical $L1_2$ phase to the formation of LPNS with the period $2M = 2\pi/|\mathbf{q}| = 3.52$. This agrees with the experimental data. Actually, the Ag_3Mg system has never been observed in the $L1_2$ structure. It immediately changes from a disordered state to a long-period state characterized by a combination of domains ordered as D0_{22} ($2M=2$) or D0_{23} ($2M=4$) and average antiphase domain period $2M$ is 3.5 [12].

An analysis of the partial contributions to the total susceptibility $\chi(\mathbf{q})$ shows that its maximum result from transitions of 18-19 and 19-18 bands. Ultimately, the geometrical features of FS will determine this maximum: in the vicinity of the point M in the Brillouin zone (BZ) there are two reasonably large electron subbands of the 18th and 19th FS layers which virtually coincide in their configuration and are separated by the vector $\mathbf{q} = (2\pi/a)[0.284, 0, 0]$.

The susceptibility $\chi(\mathbf{q})$ calculated for Al_3Ti ordered as the $L1_2$ structure along the $\langle 100 \rangle$ direction of BZ has a local maximum at $\mathbf{q} = (2\pi/a)[0.35, 0, 0]$ characterizing this system instability with respect to the formation of a long period with $2M=2.94$. An analysis of partial contributions to the total susceptibility $\chi(\mathbf{q})$ showed that this local maximum is caused entirely by the contribution from the 7-7 intraband transitions.

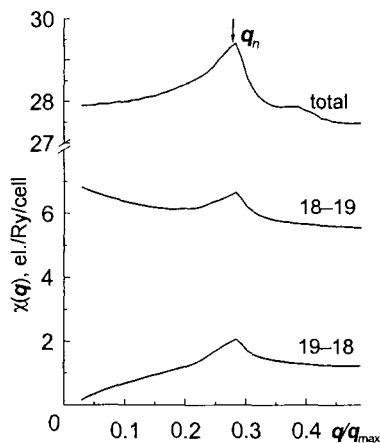


Figure 1. $\chi(\mathbf{q})$ and its partial contributions calculated for Ag_3Mg along $\langle 100 \rangle$ direction.

It should be emphasized that the low-temperature D0_{22} structure possesses a quite high degree of tetragonality $c/a=2.23$ [13]. It would, therefore be reasonable to carry out the electron-spectrum and susceptibility calculations for the $L1_2$ structure using the same tetragonality distortion as in D0_{22} , i.e., at $c/a = 1.115$. Here we should draw the attention to the following circumstance: from the general considerations one may assume that the larger the value of a period, the smaller should be the tetragonality of primitive unit cells composing this structure. Hence, in the limit of an infinitely long period this LPNS might transform into a conventional cubic $L1_2$ structure. While on the other hand, it is the simplest LPNS formed in Al_3Ti (i.e., D0_{22}) that would display maximum tetragonality. Thus, to get a comprehensive understanding of the problem we should also investigate the structures with intermediate degrees of tetragonality distortion. In this work we have treated the Al_3Ti alloy as an $L1_2$ structure with the c/a parameter varied from 1 to 1.115.

We calculated $\chi(\mathbf{q})$ for different c/a values: the feature observed in a cubic $L1_2$ structure at $\mathbf{q} = (2\pi/a)\langle 0.35, 0, 0 \rangle$ shifts to the right as the c/a value increases, and

then gradually deteriorates. When $c/a = 1.10$, a new peculiarity develops at $\mathbf{q} = (2\pi/c) \langle 0.42, 0, 0 \rangle$. For the experimental tetragonality this feature corresponds to the vector $\mathbf{q} = (2\pi/c) \langle 0.46, 0, 0 \rangle$ (Fig. 2) which conforms to the average period $2M=2.2$. All the vector values cited above could be matched with the respective overlapping FS patches divided by them.

To summarize, we may conclude that in alloys with commensurate long-period states, as well as in systems with incommensurate LPNS, the electronic structure features, in particular the local FS geometry, play a decisive role in the formation and stabilization of long-period states.

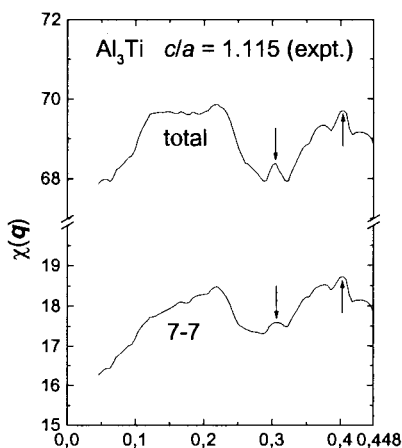


Figure 2. $\chi(q)$ and its partial contributions calculated for Al_3Ti along $\langle 100 \rangle$ direction ($c/a=1.115$).

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CHROMATIC POLARIZATION CONVERSION OF TERAHERTZ RADIATION BY A DENSITY-MICROSTRUCTURED TWO-DIMENSIONAL ELECTRON SYSTEM

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Results of a theoretical investigation of the chromatic polarization conversion of the electromagnetic wave in a density-modulated two-dimensional (2D) electron system are presented. Numerical calculations are performed with the characteristic parameters of an actual 2D electron system in the electron inversion layer on p-Si at the terahertz frequencies.

1 Introduction

Conversion of electromagnetic wave (EW) polarization provides an efficient and powerful method for diagnostics of media and structures with reduced symmetry (e.g. anisotropic crystals, media with natural and artificial gyrotropy, periodic structures, solid-state surfaces and thin films). On the other hand, such media and structures can be used as polarization converters. The conversion of the polarization in surface layers and thin films is usually small [1,2] and achromatic because in this case the region of interaction of the EW with the polarization active medium is small and the interaction itself is non-resonant. However, the effect may increase substantially (resonantly) and the polarization converted radiation becomes colored when the external EW excites eigen-oscillations on optically active surface or in an optically active film. For example, under the non-uniform cyclotron resonance excitation in two-dimensional (2D) electron system, high conversion efficiency can be reached [3].

Due to the symmetry constraints in a 2D electron system with a periodically modulated electron density, one can anticipate that strong chromatic conversion of the EW polarization will occur due to resonant coupling between the EW and plasma oscillations even without dc magnetic field applied. The theory of EW polarization conversion in the 2D electron system with a rectangular electron density profile was developed within the first principles electromagnetic approach [4]. In this paper we employ this theory to analyze the chromatic polarization conversion of terahertz (THz) radiation in such systems.

2 Theoretical model

We suppose a 2D electron plasma is located in the $y = 0$ plane at the interface between media with dielectric constants ε_1 (for $y < 0$) and ε_2 (for $y > 0$). The equilibrium surface electron density in the plane of the 2D system is a periodic function of the position x , $N_s(x) = N_s(x+L)$: $N_s(x) = N_A$ if $0 < x < w$, and $N_s(x) = N_B$ if $w < x < L$, where N_A and N_B are constants. A plane uniform EW with electric field $E^{\text{ext}}(r, t) = E^{(0)} \exp(kr - i\omega t)$, where $E^{(0)}$ is the complex-valued amplitude, is incident onto 2D electron system from the medium 2 at an angle θ to the y axis. The plane of incidence forms an angle φ with the direction of the periodicity of the structure (i.e. with x - y plane in the chosen coordinate system). Therefore the in-plane components of the wavevector k can be expressed as $k_x = k_0(\varepsilon_2)^{1/2} \sin\theta \cos\varphi$ and $k_z = k_0(\varepsilon_2)^{1/2} \sin\theta \sin\varphi$, where $k_0 = \omega/c$.

We assume that the incident EW has a linear polarization so that the electric field vector $E^{(0)}$ resides in the plane of incidence. We describe the response of 2D electron plasma on segments $0 < x < w$ and $w < x < L$ in local approximation (Drude model) by the surface conductivities in the form $\sigma_{A,B} = (e^2 N_{A,B} \tau / m^*) / (1 - i\omega\tau)$, where e and m^* are the electron charge and effective mass, τ is the phenomenological relaxation time.

We are interested here in resonant interaction between incident EW and plasma oscillations in the 2D electron system. As it is well-known [5], the plasmon wavelengths in 2D electron system are several orders of magnitude shorter than the wavelength of the EW of the same frequency. To ensure a resonant coupling between the EW and plasma oscillations, the period of the structure has to be of the order of the plasmon wavelength, which means that $L \ll 2\pi/k_0$. In this case, only transmitted and reflected EWs of the zero diffraction order survive at distances much longer than the EW wavelength away from 2D electron system.

Theory [4] allows us to calculate the power conversion coefficients as ratios of the components of the energy flux vectors normal to the plane of the 2D system at zero order of diffraction as

$$T_{pp} = \frac{P_{y,p}^{(1)}}{P_{y,p}^{(0)}}, \quad T_{sp} = \frac{P_{y,s}^{(1)}}{P_{y,p}^{(0)}}, \quad R_{pp} = \frac{P_{y,p}^{(2)}}{P_{y,p}^{(0)}}, \quad R_{sp} = \frac{P_{y,s}^{(2)}}{P_{y,p}^{(0)}},$$

where the superscripts 0, 1 and 2 refer to the incident, transmitted and reflected waves, respectively, and the subscripts p and s correspond to waves with p and s polarization (in the latter case the electric field vector of the EW is perpendicular to the plane of incidence).

3 Results and discussion

It was shown in [4] that at a certain angle of incidence $\theta > \theta_R$, where $\theta_R = \sin^{-1}(\varepsilon_1/\varepsilon_2)^{1/2}$ is the total internal reflection (TIR) angle ($\varepsilon_2 > \varepsilon_1$), the polarization

conversion coefficient R_{sp} reaches unity if electron scattering in 2D system is ignored. Almost total conversion takes place practically at every angle $\theta_k < \theta < 90^\circ$ and in a wide range of variation of the azimuthal angle φ . Polarization conversion efficiency steeply drops down to zero in the two limits when the angle of incidence approaches θ_R and at exactly grazing incidence ($\theta = 90^\circ$).

Here we present further results on the angle dependence of the polarization conversion spectra. It follows from Fig.1 that the resonant frequencies

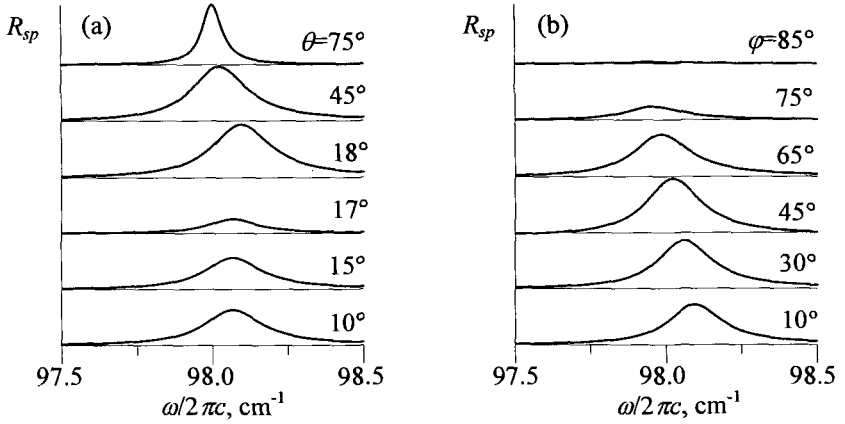


Figure 1. Polarization conversion resonance curves (a) for different angles of incidence when $\varphi=45^\circ$ and (b) for different azimuthal angles φ when $\theta = 45^\circ$. $\Delta n_s=0.5$, $(N_A+N_B)/2=3\times 10^{12}\text{cm}^{-2}$, $w=L/2$, $m^*=0.2m_0$, where m_0 is the free electron mass, $1/\tau = 0$. The total internal reflection angle $\theta_R \cong 17.2^\circ$ for the structure with $\varepsilon_1=1$, $\varepsilon_2=11.45$. The resonance curves are offset by unity.

slightly change with angles θ and φ for $\theta > \theta_R$. We attribute this dispersion of the resonant frequency to the spatial confinement of the EW field that takes place in medium l in the TIR regime.

In Fig. 2 we show the dependence of azimuthal angle $\varphi_{\max}$ at which the maximum polarization conversion takes place on the angle of incidence for different ratios of dielectric constants $\varepsilon_2/\varepsilon_1$. It is seen that $\varphi_{\max}=45^\circ$ at $\theta=0$ for any value of the contrast ratio. The value of $\varphi_{\max}=45^\circ$ at $\theta=0$ is also independent of a particular profile of electron density distribution in 2D system as well as the modulation factor $\Delta n_s=(N_A-N_B)/(N_A+N_B)$. At $\theta \neq 0$ the value of $\varphi_{\max}$ is smaller than 45° . A smaller contrast ratio corresponds to smaller $\varphi_{\max}$. The value of $\varphi_{\max}$ is equal to zero at the total reflection angle $\theta=\theta_R$ because, in this case, the in-plane component of electric field in the plane of 2D electron system vanishes.

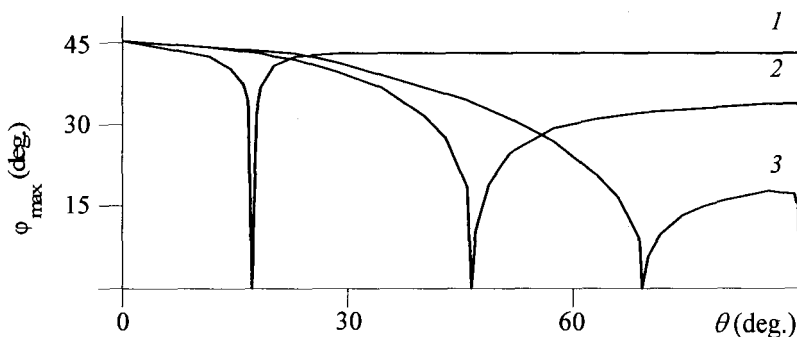


Figure 2. Azimuthal angle $\varphi_{\max}$ for the maximum polarization conversion coefficient R_{sp} versus angle of incidence θ for different values of $\varepsilon_2/\varepsilon_1$: 11.45/1 (1), 11.45/6. (2), 11.45/10. (3).

Note that the solution of the problem of the incidence of an s -polarized EW onto a periodic density-modulated 2D electron system gives the same values for the polarization conversion coefficients ($R_{\text{sp}} = R_{\text{ps}}$) in the TIR regime. This attests to a reciprocal character of the polarization conversion process for $\theta > \theta_R$.

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EXCITON-PHONON COUPLING OF LOCALIZED QUASI-2D EXCITONS IN SEMICONDUCTOR QUANTUM WELL HETEROSTRUCTURES

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We calculate the lateral size dependence of Huang-Rhys factors for localized quasi-2D excitons interacting with phonons in semiconductor QW heterostructures. The Huang-Rhys factors increase with decreasing the localization area. This indicates an enhancement of exciton-phonon interactions with decreasing the localization area of quasi-2D excitons.

1 Introduction

Semiconductor quantum-well (QW) heterostructures attract considerable attention of experimentalists due to their unique physical properties and their applications in modern nanoelectronics as various light emitting devices and logic devices for quantum information processing. There are systems among them where the fluctuation of the well thickness produces the fluctuation of the translational energy of quasi-2D excitons making them localized at energetically local minimum sites in island-like structures of several tens nanometers in diameter [1]. These localized excitonic states can be regarded as *weakly* confined quantum dot (QD) like states. One dimension of the confinement is defined by the QW width (typically from one to several monolayers), while the other two lateral dimensions are defined by the effective size of the island. Recent experiments have demonstrated a key role of phonon interactions in such systems for both III-V and II-VI heterostructures [2,3]. In particular, acoustic phonons were shown to be responsible for the non-Lorentzian behavior of the exciton emission line with increasing temperature [2], whereas the interactions with optic phonons were demonstrated to lead to the formation of strong coupling polarons [3].

In this paper, we present the lateral size dependence of Huang-Rhys factors for the QW heterostructures with the localized quasi-2D excitonic states. The Huang-Rhys factor is a quantity representing the coupling strength of a localized particle with phonons [4]. All exciton-phonon interaction mechanisms are analyzed. They are the polar optic (Froehlich) interaction, the optic deformation potential, the^{*} acoustic deformation potential, and the acoustic piezoelectric interaction. We would

like to emphasize that, contrary to QD nanocrystallites where the adiabatic Huang-Rhys concept is either inapplicable at all due to the strong inharmonicity [5] or sometimes applicable in the *strong* confinement regime [6], we deal with the more simple situation where the quasi-2D exciton is *weakly* confined in the lateral plane of a *thick* planar superlattice of two semiconductors with *similar* dielectric and elastic properties and different band gaps. Typical examples are InAs-GaAs, CdTe-ZnTe, etc. [1-3].

2 The model

In the case of QW heterostructures, the electron and hole of an exciton are well confined within the layer since the band gap discontinuity is quite large, especially for III-V heterostructures. On the other hand, dielectric and lattice properties of group III (II) and group V (VI) semiconductors (dielectric permittivities, lattice constants, elastic moduli) are in close proximity in their values [7]. Therefore, we model our system by the localized quasi-2D 1S-exciton interacting with bulk-like phonon modes in the QW with infinite potential barriers. We describe such an excitonic state by quasi-2D wave function

$$|\mathbf{R}_0\rangle = v_0 \sum_{\tilde{\mathbf{r}}_e, \tilde{\mathbf{r}}_h} f(\mathbf{R}_{||} - \mathbf{R}_0) F_{1S}(\mathbf{r}_{e||} - \mathbf{r}_{h||}, z_e, z_h; \alpha, \beta) a_{c\tilde{\mathbf{r}}_e}^+ a_{v\tilde{\mathbf{r}}_h} |0\rangle \quad (1)$$

with in-plane Gaussian distribution $f(\mathbf{R}_{||} - \mathbf{R}_0) = \exp[-(\mathbf{R}_{||} - \mathbf{R}_0)^2 / 2\xi^2] / \xi\sqrt{\pi}$ of the exciton centre-of-mass motion around the localization centre at point $\mathbf{R}_0$ and the in-plane exciton envelope F_{1S} of an exponential form with two variational parameters α and β [8]. Operator $a_{c\tilde{\mathbf{r}}_e}^+$ creates the electron in the conduction band at point $\tilde{\mathbf{r}}_e$, operator $a_{v\tilde{\mathbf{r}}_h}$ annihilates the electron, producing the hole in the valence band at point $\tilde{\mathbf{r}}_h$; $|0\rangle$ is the ground state of the system, v_0 is the volume of the unit cell, $\mathbf{R}_{||} = (m_e \mathbf{r}_{e||} + m_h \mathbf{r}_{h||}) / (m_e + m_h)$ is the in-plane excitonic centre-of-mass coordinate with m_e (m_h) being the electron (hole) effective mass. The parameter ξ in $f(\mathbf{R}_{||} - \mathbf{R}_0)$ is the excitonic localization length. The quantity $2\sqrt{2\ln 2}\xi$ may be considered as a typical lateral size of the localization area of the excitonic centre-of-mass or, in other words, as a typical lateral size of QD.

The total Hamiltonian of the system is of the form

$$H = E_0 B^+ B + \sum_{\mathbf{q}, l} \hbar \omega_{\mathbf{q}l} (b_{\mathbf{q}l}^+ b_{\mathbf{q}l} + 1/2) + B^+ B \sum_{\mathbf{q}, l} M_{\mathbf{q}l} (b_{\mathbf{q}l}^+ + b_{-\mathbf{q}l}), \quad (2)$$

where B^+ (B) are the creation (annihilation) operators of the localized quasi-2D exciton with energy E_0 , $b_{\mathbf{q}l}^+$ ($b_{\mathbf{q}l}$) are those for the phonon of branch l with momentum $\mathbf{q}$ and energy $\hbar \omega_{\mathbf{q}l}$. The first two terms of the Hamiltonian describe the

exciton and phonon subsystems. The third one describes their interaction represented by diagonal interaction matrix element

$$M_{q_l} = \langle \mathbf{R}_0 | w_e(\mathbf{q}, l) e^{i\mathbf{q} \cdot \mathbf{r}_e} - w_h(\mathbf{q}, l) e^{i\mathbf{q} \cdot \mathbf{r}_h} | \mathbf{R}_0 \rangle, \quad (3)$$

where $w_{e,h}(\mathbf{q}, l)$ depends on the type of the exciton-phonon interaction (enumerated by l). Specifically, $w_{e,h} = -e\sqrt{2\pi\hbar\omega_0(1/\varepsilon_\infty - 1/\varepsilon_0)}/L^3(1/q)$ for the polar optic (Froehlich) interaction, $w_{e,h} = -D_o^{(e,h)}\sqrt{\hbar/2\omega_0 L^3\rho}$ for the optic deformation potential, $w_{e,h} = -E_d^{(e,h)}\sqrt{\hbar q/2u_{LA}L^3\rho}$ for the acoustic deformation potential, and $w_{e,h} = -(8\pi ee_{14}/\varepsilon_0)\sqrt{\hbar/2u_{LA,TA}L^3\rho}(e_x q_y q_z + e_y q_z q_x + e_z q_x q_y)/q^{5/2}$ for the acoustic piezoelectric interaction, where L , ρ and $\varepsilon_{\infty,0}$ are the linear size, the density and the dynamic (static) dielectric permittivity of the quantization area, respectively, e is the electron charge, $D_o^{(e,h)}$ and $E_d^{(e,h)}$ are, respectively, the optic and acoustic deformation potential coupling constants, e_{14} is the electromechanical piezoelectric constant of zinc-blend type crystals, ω_0 is the dispersionless frequency of optic vibrations, $u_{LA,TA}$ is the velocity of LA (TA) acoustic vibrations with unit polarization vectors $\mathbf{e}(LA) = (q_x, q_y, q_z)/q$, $\mathbf{e}(TA1) = (q_y, -q_x, 0)/\sqrt{q_x^2 + q_y^2}$ and $\mathbf{e}(TA2) = (-q_x q_z, -q_y q_z, q_x^2 + q_y^2)/q\sqrt{q_x^2 + q_y^2}$ [7,8].

The Huang-Rhys factor for a specific exciton-phonon interaction mechanism is

$$S_l(T) = \sum_q \frac{|M_{q_l}|^2}{(\hbar\omega_{q_l})^2} (2n_{q_l} + 1), \quad (4)$$

where n_{q_l} is the phonon occupation number and M_{q_l} is defined by Eq.(3) with $|\mathbf{R}_0\rangle$ given by Eq.(1). Below, we calculate the dependence of $S_l(0)$ on the lateral size of the exciton localization area, or on the lateral size of QD.

3 Numerical results

We calculated the size dependence of the zero-temperature Huang-Rhys factors (4) using parameters of GaAs [7]. Fig. 1(a) shows the optic Huang-Rhys factors of 2D-excitons (flat dot) as a function of the QD lateral size. The Froehlich interaction is seen to dominate over the optic deformation potential interaction (caused by the heavy hole interaction in a p-like valence band). The total optic Huang-Rhys factor gradually increases with the decreasing QD lateral size.

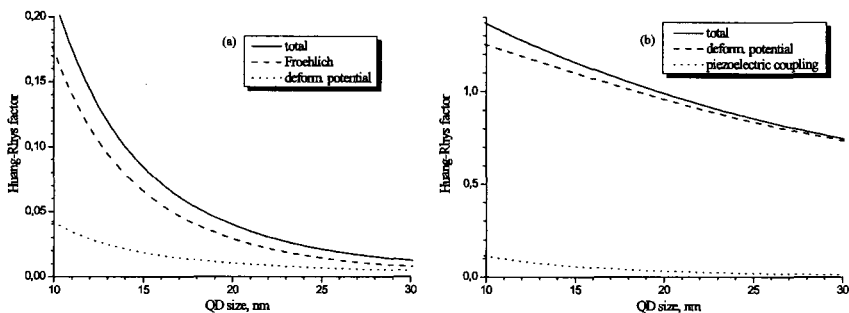


Figure 1. Optic (a) and acoustic (b) zero-temperature Huang-Rhys factors of localized 2D-excitons.

The acoustic Huang-Rhys factor for localized 2D-excitons is shown in Fig. 1(b). The acoustic deformation potential interaction totally prevails over the acoustic piezoelectric interaction. The total acoustic Huang-Rhys factor is ~ 1 and increases with the decreasing QD size. This indicates rather strong exciton-acoustic-phonon coupling which further enhances with the decrease of the QD lateral size.

In conclusion, our calculations show an enhancement of the exciton-phonon interactions in quasi-2D QD-like islands in QW heterostructures. This entails the respective increase of the excitonic dephasing rate. Our conclusion is valid unless the quasi-2D exciton may be considered as *weakly* confined in the lateral plane.

Acknowledgements

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LATTICE MATCHING BETWEEN BULK Ru_2Si_3 AND NANOCRYSTALLINE RuSi_2

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An analysis of geometrical matching between bulk Ru_2Si_3 and nanocrystalline RuSi_2 has been performed for three types of its lattice, namely for α -, β -, and γ -phase. The best matching has been found for α - RuSi_2 . This is characterized by the common unit cell area of 1.86 nm^2 and 0.04 % diagonal lattice mismatch.

1 Introduction

Semiconducting transition-metal silicides, which are characterized by good compatibility with the conventional silicon technology, attract much attention because of the prospects for optoelectronic and thermoelectric applications [1]. Fe-Si and Ru-Si systems are the most promising ones among them [2-6]. Until recently it has been believed that only one equilibrium compound, Ru_2Si_3 , is present in the silicon-rich part of the ruthenium-silicon phase diagram [7]. Lately a single-crystalline ruthenium disilicide RuSi_2 has been experimentally observed in the form of inclusions, about 500 nm in size, in Ru_2Si_3 single crystals grown by the zone melting technique [8]. Unfortunately, no structural characterization has been done due to the small size of the inclusions. Nevertheless, by analogy with the Fe-Si system in which the disilicide is the most promising compound, the structural and electronic properties of α -, β -, and γ - RuSi_2 , have been calculated by means of ultrasoft pseudopotential and full-potential linearized augmented plane wave methods [9].

In this paper, we analyze geometrical matching between bulk Ru_2Si_3 and nanocrystalline RuSi_2 for three types of its lattice in order to predict which phase, α -, β -, or γ - RuSi_2 , has the best matching probability. We then compare the results of our calculations with the available experimental data.

2 Computational details

The structural properties of RuSi_2 have been calculated for three crystalline phases: high-temperature tetragonal ($P4/mmm$) α -phase, orthorhombic ($Cmca$) β -phase, and metastable pseudomorphic cubic ($Fm3m$) γ -phase with 3, 24 and 3 atoms in the unit cell, respectively [9]. Table 1 summarizes the optimized lattice constants of the ruthenium silicides.

Table 1. The optimized lattice constants a , b , and c of the silicon rich ruthenium silicides.

Silicide	a (Å)	b (Å)	c (Å)
Ru_2Si_3	10.991	8.905	5.495
α - RuSi_2	2.836	2.836	5.209
β - RuSi_2	10.053	8.028	8.124
γ - RuSi_2	5.606	5.606	5.606

An algorithm for a choice of the most probable combinations of the RuSi_2 embedding in Ru_2Si_3 matrix has been proposed. We proceeded from the idea that positions of atoms in Ru_2Si_3 and RuSi_2 should be the same in some so-called basic points. As the lattice constants of the embedded crystals and the matrix are different, the most probable matching should occur when a block of several RuSi_2 unit cells has common basic points with a block of several Ru_2Si_3 unit cells. Thus, at the plane where Ru_2Si_3 structure is tangent to RuSi_2 one, a common diagonal of the crystals block with the size $k \times l$ of a RuSi_2 should coincide (with a given accuracy) with a common diagonal or a side of the crystal block of the size $n \times m$ of Ru_2Si_3 . This means that the crystal lattices can be joined in the appropriate plane with a turn of the unit cells. The algorithm has been realized within a computer program, in which various combinations of k , l , n , m are calculated by means of elementary exhaustion with the given accuracy.

3 Results and discussion

The best lattice matching was found between 4 Ru_2Si_3 unit cells and 16 α - RuSi_2 unit cells as it is shown in Fig. 1a. It is characterized by the common unit cell area of about 1.86 nm^2 with the axis mismatches of 25 %, 5 %, 0.04 % for b and c axis and the common diagonal, respectively. In case when the diagonal of one Ru_2Si_3 unit cell coincides with the side of the block of two α - RuSi_2 unit cells the common unit cell area is about 0.2 nm^2 with the diagonal mismatching of 0.4 %, as illustrated in Fig. 1b. The best matching for orthorhombic β - RuSi_2 is characterized by the common unit cell area of about 4.21 nm^2 with the axis mismatching 8 %, 40 %, and 0.02 % for a and c axis and the common diagonal, respectively. No reasonable match has been found between Ru_2Si_3 and cubic γ - RuSi_2 .

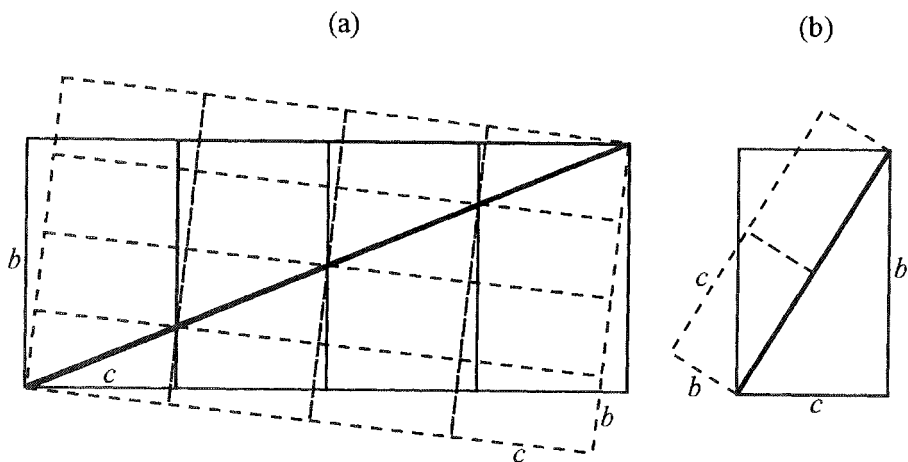


Figure 1. Projection of Ru_2Si_3 unit cells onto yz plane (solid lines) together with a possible position of $\beta\text{-RuSi}_2$ unit cells (dashed lines) for different matching cases.

Our results are mostly confirmed by the experimental data [8]. Fig. 2 demonstrates a high resolution TEM micrograph of a RuSi_2 inclusion in the Ru_2Si_3 bulk crystal grown by the zone melting technique. The ordered atomic layers from a distance of about $3.65 \text{ \AA}$ are clearly visible. So, we can observe nanocrystalline tetragonal $\alpha\text{-RuSi}_2$ with $c = 5.209 \text{ \AA}$.

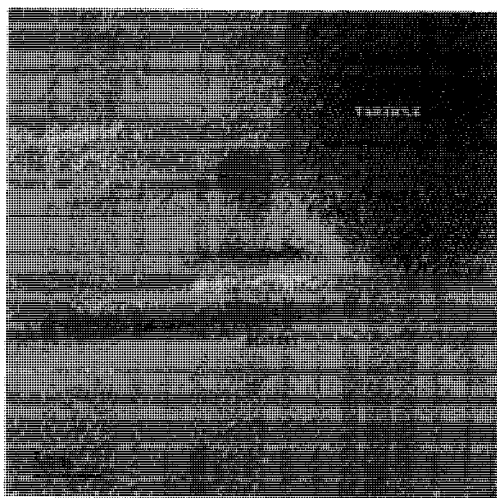


Figure 2. High resolution TEM micrograph of a RuSi_2 inclusion in the Ru_2Si_3 bulk crystal.

4 Conclusion

An analysis of geometrical matching between bulk Ru_2Si_3 and nanocrystalline RuSi_2 has been performed for three types of ruthenium disilicide, namely for α -, β -, and γ -phase. The best matching was found for α - RuSi_2 . This is characterized by the common unit cell area of about 1.86 nm^2 with the axis mismatches of 25 %, 5 %, and 0.04 % for b and c axis and the common diagonal, respectively.

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CHEMISTRY OF NANOSTRUCTURES

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NANOCLUSTER SUPERLATTICES GROWN AT SOLUTION SURFACES

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Gold (Au) nanocrystals with hydrophilic surfactant modified surfaces were assembled into three-dimensional (3D) lattice arrangements at an air/aqueous suspension interface. The electrolyte concentration and the temperature controlled the assembly rate of the nanoclusters. Under optimum conditions, micrometer-sized faceted structures were grown at the suspension surface. TEM observations show that each nanocluster assembly formed a single crystal arrangement with a hexagonal close-packed (HCP) structure where $a = 5.2$ nm. As the temperature rises, the attractive interactions between the nanoclusters increased, which indicates that the driving force of the assembly is due to the hydrophobic effect. The hydrophobic effect is a result of the hydrophilicity-hydrophobicity conversion as the pH decreases.

1 Introduction

An interesting artificial solid in material science is a three-dimensional (3D) periodical array of nanoclusters or a 3D nanocluster superlattice because the electronic structure may be customized by controlling the core size, the surface coverage thickness, and/or the packing arrangement. Recently, 3D nanocluster superlattices were successfully synthesized using a spontaneous assembly process [1-14]. In 1989, Bentzon *et al.* reported that Fe_2O_3 nanoclusters spontaneously formed 3D close-packing arrangements by drying the nanocluster-containing organic suspension [1]. Afterwards Krätschmer reported that fullerenes form close-packing lattices when drying fullerene-containing benzene [2]. Since then, various metal or semiconductor nanocluster superlattices have been synthesized using similar self-assembly processes [3-12].

Recently, we found that hydrophilic nanoclusters are excellent components for 3D superlattices since the assembly rate of the nanoclusters, i.e. the growth rate of superlattices, is widely tunable by adjusting the concentration of the electrolyte. In non-equilibrium conditions there is abrupt growth, but under equilibrium conditions the nanoclusters grow extremely slow [13,14]. During equilibrium growth two processes can improve the 3D superlattice arrangements. The first process is that non-uniform particles are repelled towards the boundaries of the superlattice if the lattice contains component particles of various sizes [14,15]. The second is the diffusive nature of particles in a suspension, a particle trapped inside a metastable

site can be released back into suspension and diffuses about the lattice surface until the most stable position is found [15]. These processes narrow the size distribution inside the lattice, remove lattice defects, and improve the lattice symmetry. In this study, 3D superlattices were synthesized using Au nanocrystals whose surfaces were modified with hydrophilic surfactants. Under optimal electrolyte concentration and temperature, micrometer-sized high-quality lattices were obtained.

2 Experimental

Au nanoclusters were prepared by the following procedure. First, 0.8 mmol of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, dissolved as 2 % (w/v) aqueous solution, was mixed with 120 ml of methanol containing 1.6 mmol of mercaptosuccinic acid (MSA). Then while vigorously stirring and ultrasonically irradiating, 27 ml of a 0.3 M aqueous sodium borohydride (NaBH_4) solution was added. After the reaction, Au nanocrystals with a MSA monolayer on the surface were obtained. The solvent was decanted after centrifugation at 2460 g, which corresponds to 5000 rpm for the Kubota 1720 centrifuge. The samples were then washed 5 times with a 30 % (v/v) water-methanol solution by repeating re-suspension with a sonicator and re-centrifugation, and finally dialyzed to remove unbound MSA, Au-MSA complexes, and other impurities.

The nanoclusters were assembled by the following procedure. First, the nanoclusters were dispersed in distilled water. Then, hydrochloric acid (HCl) was added to weaken the repulsive interactions among the nanoclusters. Afterwards, the suspension was stored in a closed glass bottle to prevent the solvent from evaporating. By growing the superlattices under equilibrium conditions, the nanoclusters were assembled into lattice arrangements at the suspension surface (Fig. 1). Typical conditions for equilibrium growth were a HCl concentration between 0.2 – 0.3 M and a temperature between 20 – 30 °C and the lattices appeared in 3 – 5 days.

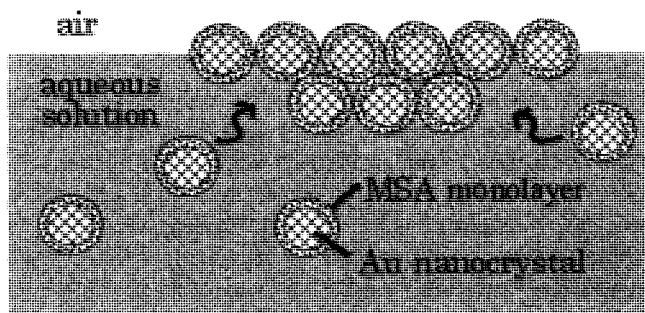


Figure 1. Assembly of the Au nanoclusters at the air/aqueous solution interface.

The size of the nanoclusters was evaluated by dynamic light scattering of the nanoclusters dispersed in distilled water using a Malvern HPPS with an incident beam of the 633 nm line of He-Ne laser. The structural characterization of the nanocluster assemblies was performed using a scanning electron microscope (SEM: Philips XL-20LaB6) operated at 20 kV, a transmission electron microscope (TEM: Hitachi H-8100) operated at 200 kV, and an X-ray diffractometer with $\text{CuK}\alpha$ radiation (Rigaku RINT-2000).

3 Results and discussion

Fig. 2 shows the nanocluster size distribution obtained from the dynamic light scattering measurement. From the spectrum, the average diameter is estimated to be 5.0 nm. When the thickness of surface MSA monolayer (~ 0.7 nm) is accounted for, the average diameter of the Au cores is estimated to be ~ 3.6 nm, which corresponds to the average core size obtained from our previous TEM observations [14].

Fig. 3 shows a SEM image of the nanocluster assemblies grown under equilibrium conditions. The assemblies form crystal like shapes with clear facets with widths and thicknesses between $0.6 - 16 \mu\text{m}$ and $0.2 - 5 \mu\text{m}$, respectively. Fig. 4 shows a typical TEM image of the superlattice and when the edges are closely examined nanoclusters that form close-packed arrangements are clearly identified. Fig. 5 shows a transmission electron diffraction (TED) pattern of the superlattice. TEM and TED studies indicate that each superlattice consists of nanoclusters, which form single crystal arrangements. After analyzing numerous TED patterns, it was concluded that all superlattices show the same hexagonal patterns with lattice constants of 5.2 nm for the hexagonal close-packed (HCP)

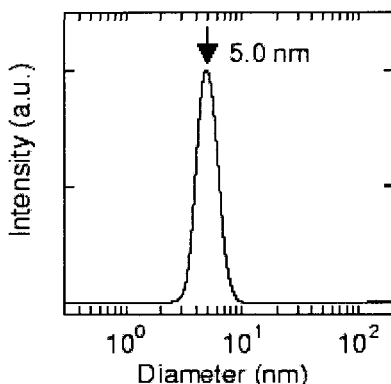


Figure 2. The dynamic light scattering measurement of the cluster size distribution when the clusters were dispersed in distilled water at 25°C.

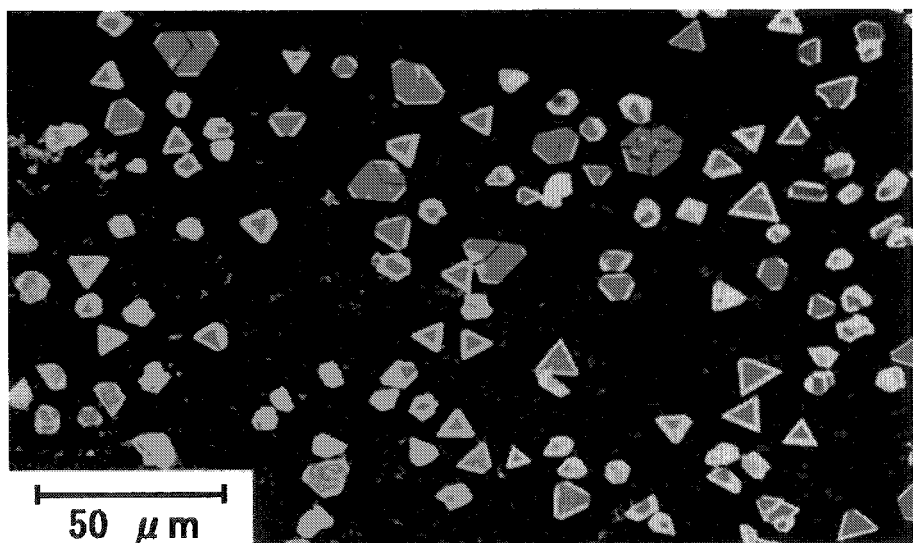


Figure 3. SEM image of the Au nanocluster superlattices. The samples were grown from a suspension at 22°C.

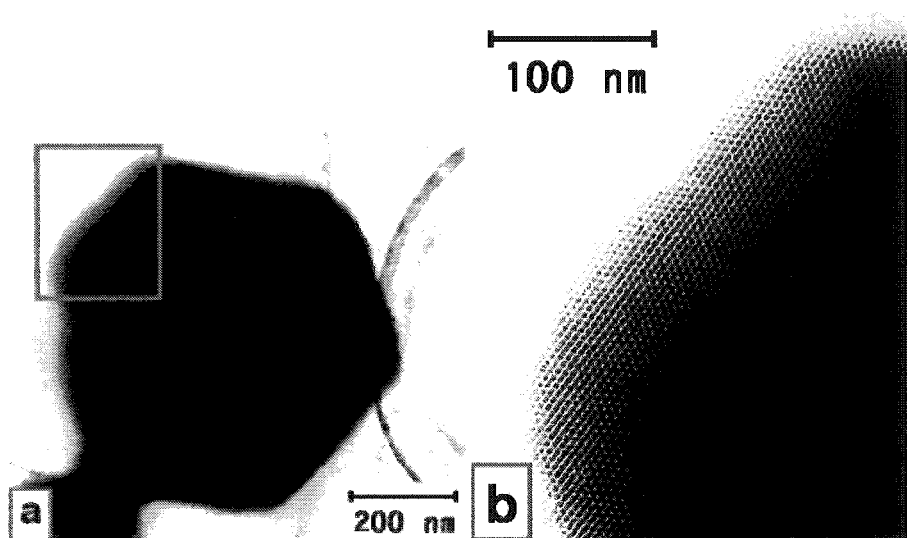


Figure 4. TEM image of the Au nanocluster superlattice: (a) overall shape, and (b) magnification of the part outlined in image (a). The superlattice was grown from a suspension at 22°C. The sample was scooped with a specimen grid covered by a perforated carbon film.

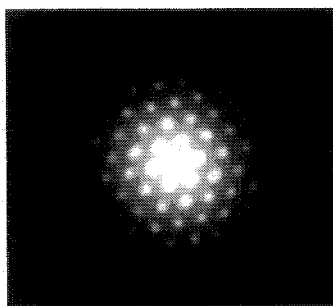


Figure 5. Typical TED pattern of the superlattice.

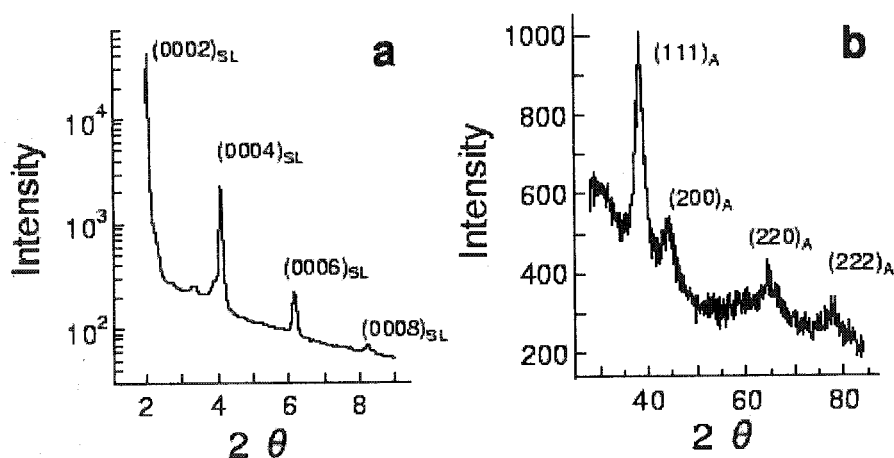


Figure 6. XRD pattern from (a) the superlattices, and (b) the component nanocrystals. The indices denoted in figures (a) and (b) are those of the HCP structure with $a = 5.2$ nm and the FCC structure with $a = 0.41$ nm (the crystal structure of bulk Au), respectively. The superlattices were grown from a suspension at 22°C.

lattice and 12.9 nm for the face-centered cubic (FCC) lattice. Assuming a close-packing hard sphere model, the diffraction patterns from a [0001] oriented HCP lattice or a [111] oriented FCC lattice explain the TED patterns. The diameters of the component nanoclusters calculated from these lattice constants are 5.2 nm and 9.1 nm in the HCP and FCC lattices, respectively. After estimating the cluster size from dynamic light scattering measurements (Fig. 1), the packing structure is determined to be the HCP structure. Fig. 6 shows the X-ray diffraction (XRD) pattern of the superlattices. The peak positions are explained by the above HCP structure, but not the above FCC structure [16].

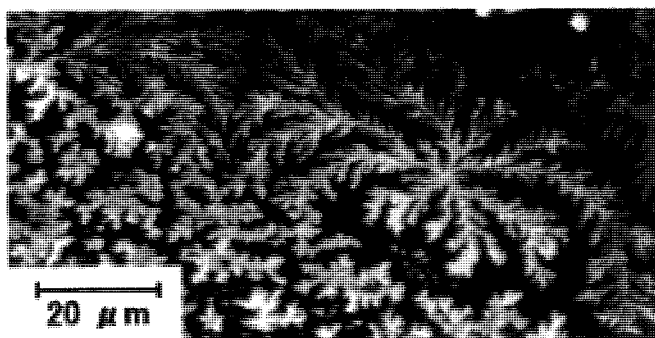


Figure 7. SEM image of the Au nanocluster aggregates grown at an air/suspension interface at 35°C. The HCl concentration in the suspension was adjusted to 0.3 M and the sample was scooped with a silicon wafer.

The assembly process of the nanoclusters is very sensitive to the temperature of the suspension. High-quality lattice arrangements were obtained between 20 and 30°C, and an HCl concentration between 0.2 and 0.3 M. At temperatures higher than 30°C, the nanoclusters form fractal patterns (Fig. 7), which results from the diffusion-limited aggregation (DLA) process of particles on the suspension surface [17]. This indicates that the nanoclusters are strongly attracted as the temperature rises, but assembly is not observed for temperatures less than 20°C. The increasing attractive interaction with temperature is characteristic of the interaction between hydrophobic surfaces in water [18,19]. Therefore, the assembly of the nanoclusters seems to be due to the hydrophobic effect [20], which results from the nanocluster surfaces being converted from hydrophilic to hydrophobic. Assuming that the ionization of the MSA surface layers is significantly suppressed by decreasing the pH, this conversion can be understood and the conjecture also explains why nanoclusters are assembled at the aqueous solution surface only after HCl is added.

4 Summary

Micrometer-sized 3D superlattices of Au nanoclusters were grown at an aqueous solution surface. The average diameter of the component nanoclusters including the surface MSA layer was ~ 5.0 nm. While growing, the HCl concentration and the temperature controlled the interaction between the nanoclusters. Under equilibrium conditions, the nanoclusters assembled at the suspension surface into single-crystal arrangements with HCP structures where $a = 5.2$ nm. The assembly rates of the nanoclusters increased as temperature increased, indicating that the assembly of the nanoclusters is due to the hydrophobic effect, which results from the ionization of the nanocluster surfaces being suppressed.

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EXCITONICS OF I-VII SEMICONDUCTORS

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Excitonic absorption and photoluminescence (PL) of nanoparticles of zincblende structured I-VII semiconductors (CuX and AgI , $\text{X} = \text{Cl}, \text{Br}, \text{I}$) are briefly reviewed. In Cu-stabilized AgI thin films formed by ambient iodination, exciton absorption sensibly monitors the film growth, where Cu favors enhanced PL involving excitons in quasi-free AgI nanoparticles. In Sb-doped AgI thin films, Sb achieves interface stabilized, more retarded AgI particle growth while causing PL due to donor-acceptor recombination.

1 Introduction

Excitons are the simplest manifestations of many-body elementary excitations in crystalline solids. These are the bound states of an electron-hole system held by a Coulomb attraction - not as strong as in a hydrogen atom but more like in positronium. The ground and excited states of an exciton are properly represented only in a two-particle band picture (Fig. 1) [1]. The process of creation, stabilization and recombination of excitons could well be conveniently investigated through ambient optical absorption and photoluminescence in I-VII compounds.

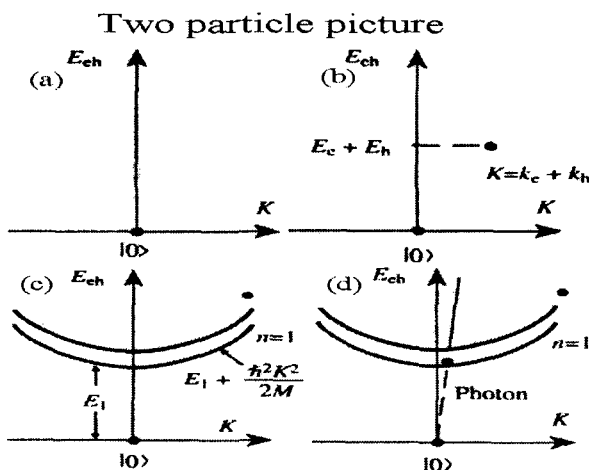


Figure 1. Exciton energy levels. (a) ground state, (b) excited state, (c) correlated exciton and (d) optical absorption. E 's are energies, M =mass, K =momentum.

Monohalides of copper and silver - especially CuCl, CuBr, CuI, AgI and AgBr belong to this class. The first four of the above materials are characterized by mutual tetrahedral bonding between metal and halogen leading to an open 3D structure namely zincblende structure and direct electronic energy band gap similar to that of GaAs (III-V) and CdTe (II-VI) [2]. Unlike the bonding in covalent semiconductors, there is a healthy mix of ionic and covalent bonding in the manner of a weakly covalent structure in I-VII compounds. A large concentration of highly mobile Frenkel defects makes these materials 'superionic conductors' at fairly high temperatures. Thus, the unique semiconductor-superionic conductor combination is crucial in understanding both ion and carrier (i.e. electron and hole) dynamics and their recombination, with implications for the photographic process, gas sensing mechanism and wave-guides for optical communication.

Interestingly the formation of excitons in nanoparticles stabilized on thin films - a basic cluster formation process in thin film physics - leads to the creation of quantum dots, i.e. quasi-zero dimensional structures that confine carriers in all the three spatial dimensions, thereby enhancing applicable phenomena such as light emission and gas sensing.

2 Theory

Two quantities - Bohr radius (a_B) and binding (ground state) energy (E_{ex}) - characterize excitons in a semiconductor [3]. The dielectric constant (ϵ) of the semiconductor 'stabilizes' these two quantities through equations (1) and (2) derived in a hydrogenic model with the coulomb potential 'normalized' by ϵ , within the framework of the effective mass approximation.

$$a_B = (\hbar^2/4\pi^2 e^2)\epsilon, \quad (1)$$

$$E_{ex} = 4\pi^2 m_r e^4/2 \epsilon^2 \hbar^2, \quad (2)$$

where m_r is the reduced mass of the electron-hole pair: $m_e m_h / m_e + m_h$.

The energy spectra predicted by the hydrogenic model is a series of sharp and discrete levels right up to the continuum i.e. the conduction band. Real exciton spectra, however, have a finite, temperature dependent width (and line shape) and the peak positions are a function of size of the "quantum dot". This is the consequence of the finiteness of the nanocrystal (a macroscopic crystal is infinite) whose boundaries present a potential barrier for the motion of the carrier and whose size could be of the order of a_B . These quantum size effects as well as the confinement of carriers (either together or separately) are the basic phenomena, the consequences of which are to be understood and exploited in excitonics [3].

In the two-particle picture (Fig. 1), the optical absorption by excitons involves the conversion of a photon into an exciton, the absorption occurring at a place where phonon dispersion curve intersects the exciton dispersion curve, meeting

conservation criteria. Photoluminescence involves conversion of external photons by the medium into coupled exciton-photon states.

Photoluminescence could be due to the radiative annihilation (or recombination) of excitons to produce a free exciton peak or due to recombination of an exciton bound to a donor or acceptor impurity (neutral or charged) in the semiconductor. The free exciton spectrum generally represents the product of the polariton distribution function and the transmission coefficient of polaritons at the sample surface. Bound exciton emission involves interaction between bound charges and phonons, leading to the appearance of phonon side bands. The above-mentioned electronic properties exhibit quantum size effect in the nanometric size regime when the crystallite size becomes comparable to the Bohr radius, a_B . The basic physics of this effect is contained in the equation for confinement energy,

$$E_c = (\hbar^2/8R^2)(1/m_r) - 1.786e^2/\epsilon R - 0.248E_{Ry}^x, \quad (3)$$

$$E_c = E_{nanoparticle}^{gap} - E_{bulk}^{gap}, \quad (4)$$

where R is the nanoparticle radius.

Here E_c is the algebraic sum of the particle-in-a-box localization energy, the coulomb energy and the spatial correlation energy. A qualitative explanation of the blue shift, eq. (4), in the absorption onset observed during the formation of nanoparticles (clearly a size effect) is possible in the case of not-too-small nanoparticles [1-3]. Other significant effects of spatial confinement of charge carriers include the enhancement of carrier kinetic energies, increased efficiency of electron-hole recombination process, change in the dynamics of charge carrier trapping and enhancement of indirect exciton emission. The emission wavelengths in bulk semiconductors correlate with distances r among trapped electrons and holes as a consequence of the Coulomb interaction between trapping sites. When charge trapping sites trap electrons and holes, the Coulomb term vanishes [1,2]. A radiative tunneling model relates the wavelength of the emitted photon to the energy of the lowest delocalized state of the crystal E_x and the depths of electron and hole traps, D_+ and D_- :

$$E(h\nu_{em}) = E_x - (D_+ + D_-) + e^2/\epsilon r. \quad (5)$$

Closely spaced electron-hole pairs (small r) emit faster and at higher energies than the distant ones. In the nanocrystalline regime, r correlates with the particle size so that eq. (5) holds as relevantly discussed using the recent results on the excitonics of I-VII nanocrystals.

3 Results and discussion

Matrix-stabilized (glass, NaCl) CuCl nanocrystals is a typical zero-dimensional material, which constitutes a quantum dot system in which excitons are weakly confined [4]. Small angle X-ray scattering study has established that the resultant

blue shift of the Z_3 exciton absorption peak (see later) is inversely proportional to the square of the effective radius. Since the exciton radiative lifetime is found to be proportional to (effective radius)³, for < 5 nm particles, exciton 'superradiance' occurs for coherent excitons confined in CuCl crystals. This could be the origin of large optical nonlinearities as conveniently studied through saturation of absorption and photoluminescence of confined excitons [4]. The optical nonlinearity of nanocrystals is a function of the number of excitons created in a nanocrystal. A significant observation is that the measured saturation intensity for luminescence becomes much larger than that of absorption. Formation of biexcitons (caused by exciton-exciton interaction) also gives rise to nonlinear luminescence with recoil of one exciton.

A very interesting two-photon absorption study of ⁶³CuCl and ⁶⁵CuCl [5] has revealed that the band gap of the latter is smaller than that of the former, an observation that is counterintuitive! Both longitudinal exciton (1S exciton) and transverse polariton (1S exciton-polariton) spectra have been obtained - the first one by monitoring the free exciton luminescence from the lower polariton branch at 390 nm wavelength and the second one by measuring the intensity of second harmonic generation. More significantly, the temperature dependence of the energy gap is anomalous - *increases* upon *increasing* the temperature. Electron-phonon renormalization of the electronic structure due to a strong admixture of core-like d electrons in the valence band accounts for all these observations and serves as a firm basis for the discussion of the excitonics of I-VII nanocrystals. This explanation rationalizes all the major anomalous physical properties of these semiconductors including thermal expansion, specific heat and ionic conductivity. Indeed, as Ono *et al.* [6] have demonstrated recently, the strength of the so called *p-d* hybridization in which the *3d(4d)* states of Cu(Ag) are coupled to the *4p/5p/6p* states of Cl/Br/I in Cu and Ag halides are related to the conductivity activation energies.

CuBr also shows an anomalous temperature dependence of the energy gap. The postulate that the vibration of Cu ions leads to an increase in the gap while that of the halide ion results in a decrease in the gap is thus reasonable. These observations have an important bearing on the temperature-dependent excitonic spectra of CuBr nanocrystals.

Suyal *et al.* [7] have synthesized $\text{CuCl}_x\text{Br}_{1-x}$ ($1 \leq x \leq 0$) nanocrystals (diameter = 5 – 15 nm) in thin films by the sol-gel process, by stepwise substitution of Cl by Br, eventually achieving complete substitution to get CuBr thin films. Exciton absorption spectra show a valence band state reversal effect as *x* is increased from 0 (CuCl, with positive spin orbit coupling) to a value greater than 0.24, where the spin orbit splitting becomes negative. At *x* = 0.24, the spin orbit interaction is absent leading to triple degeneracy of the valence band top in the zincblende structure. Therefore, Z_3 excitons occur at a lower wavelength than $Z_{1,2}$ in CuBr. The postulate that the vibration of the Cu ions leads to an increase in the gap while that of halide ion results in a decrease in the gap is thus justified. The half-width of the sharper and more intense $Z_{1,2}$ excitons show a quadratic

temperature dependence, which is in agreement with Toyozowa's theory [8] predicting that

$$W = g^2(kT)^2/8\pi^2 m^* u^2, \quad (6)$$

where g is the dimensionless coupling constant, m^* is the reduced effective mass of excitons, u is the longitudinal sound velocity and k is the Boltzmann constant.

This interesting study must be extended to include: (a) an analysis of Z_3 exciton, (b) an investigation of linear and non-linear photoluminescence to look at exciton-exciton interaction and dynamics. CuBr nanocrystals embedded in a borosilicate glass matrix have been investigated by Valenta *et al.* [9] for size dependent excitonic luminescence using resonant and band-to-band excitation. They have also determined optical gain by pump-and-probe transmission measurements and amplified spontaneous emission using variable stripe length technique. The above account on excitons in CuCl and CuBr suggests that nanoparticles are almost always stabilized in a matrix, which implied a non-trivial interaction of the nanocrystal with the matrix and less than optimal physical effects for device applications. A further disadvantage of this matrix-based synthesis is that there is no scope for the study of metastable nanocrystal formation; besides essentially optimizing the non-equilibrium formation process.

In sharp contrast to CuCl and CuBr, CuI exhibits a positive temperature dependence of the band gap mainly due to electron-phonon interaction. Gogolin *et al.* [10] studied the temperature dependence of exciton peak energies in CuI quantum dots (average radius = 6 nm) embedded in a glass matrix. The $Z_{1,2}$ and Z_3 exciton peaks of the zincblende type dots as well as H_1 , H_2 exciton peak in the hexagonal type dots both show a red shift upon heating.

Sun *et al.* [11] have detected a low frequency exciton in $Rb_{0.5}Cs_{0.5}Ag_4I_5$ thin films fabricated on NaCl crystal substrates. This peak occurs at 0.9 eV at 300 K with a half width of 0.174 eV upon cooling. Peak energy and half width increase and decrease respectively in a linear manner, with a break at 107 K, the temperature at which the compound shows a normal to superionic phase ($\gamma \rightarrow \beta$) transition. For $RbAg_4I_5$ this temperature is 122 K. Exciton phonon interaction accounts for this shift and broadening of the exciton peak, while the break at 107 K is caused by partial lattice disordering at the phase transition (to the β -phase), accompanied by a large concentration of Frenkel defects and exciton scattering and Coulomb fluctuations triggered by these defects. There is a change in the exciton line shape from Lorentzian to Gaussian at the transition temperature.

One comment on the temperature dependences of the exciton line widths in CuBr and AgI based ternary compound is that it is quadratic in the former and linear in the latter case. A good spectral resolution is necessary to detect the small confinement contribution at low temperatures. Measurements with smaller dots would reveal sizeable confinement effects and photoluminescence measurements

would identify predominant channels of recombination that must be suitably retarded in order to obtain nanocrystals of an appropriate size.

We now consider the AgI nanocrystal growth on mesoporous thick films and quasi-amorphous thin film Ag 'substrates' through novel iodization reaction in a matrix free approach [12, 13]. The $Z_{1,2}$ exciton absorption band gradually evolves in the progressively iodized quasi-amorphous $Ag_{100-x}Cu_x$ ($x = 10, 20, 30$ and 40) thin films of $150 \text{ \AA}$ thickness. The almost instantaneous development of $Z_{1,2}$ exciton absorption as early as 1 minute iodination signals the formation of nanoparticles in the reactive substrate. Thus, the substrate has fairly isolated islands with a statistically arranged neighborhood for Ag i.e., these are randomly dispersed AgCu clusters [13]. The ready formation of this band due to the tetrahedral symmetry allowed dipole forbidden $4d^{10}-4d^95s$ reflects the valence band formation indicated by the formation of Z_3 exciton band with rapid kinetics of iodization leading to short range ordered $(Ag, Cu)I_4^-$ clusters. The faint double peak structure of this band is evidence of chemical bonding (and local electronic density of states) changes within a given disordered cluster before regular tetrahedral Ag-I₄ structure is stabilized. The maximum at 320 nm indicates that the requisite $p-d$ hybridization has occurred. The role played by Cu is in retarding the nucleated growth of AgI thereby exercising control over the particle size. The $Z_{1,2}$ peak energy changes with iodization time are recorded in Fig. 2. A faint rapid initial rise followed by saturation occurring at 1 hour iodization has to be understood as an attempt by the reactive matrix to restrict particle aggregation and ripening which would otherwise lead to the growth of microcrystals. As the metastable zincblende γ -AgI has to be stabilized at the expense of the stable wurtzite β -AgI, it is necessary to check 'anisotropic' growth of 'nanorod' AgI (wurtzite). Cu helps in achieving this because CuI itself has a stable zincblende structure. Thus, Cu renormalizes the static dielectric constant of AgI and stabilizes low dimensional quasi-free nanoparticles of AgI in a novel matrix-free process.

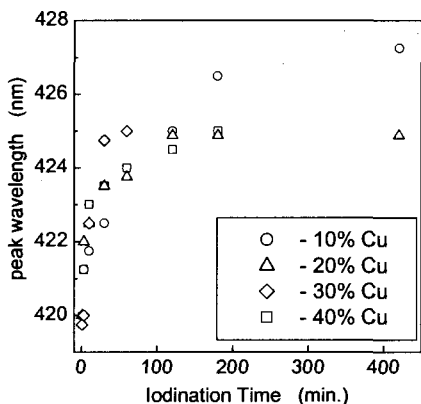


Figure 2. Peak wavelength shift of the $Z_{1,2}$ exciton of the AgI nanocrystallites formed during progressive iodination of $Ag_{100-x}Cu_x$ films. The saturation of this peak shift for all Cu-concentrations clearly depicts the formation and stabilization of the strain-induced quasi-free AgI nanoparticles.

Photoluminescence (PL) spectra of the progressively iodized Ag-Cu films under cw excitation by 330 nm light show a faint intense peak at 425 nm which grows with increasing iodination at ambient conditions. This peak is flanked by a series of weak ‘wiggles’, probably arising from weak exciton-phonon interaction. As the PL peak occurs at a wavelength very close to that of the absorption peak, it is very likely that direct recombination of photo-excited electrons close to the conduction band edge takes place with that of holes at the valence band edge [14].

The observation of exciton absorption and the associated photoluminescence in iodized quasi-amorphous $\text{Ag}_{100-x}\text{Cu}_x\text{I}$ films directly correlates the role of Cu in promoting a ‘layered plus island’ growth or S-K growth mode [15] through the formation of Ag-Cu clusters, the presence of which was evidenced in the absorption spectra during the early stage of iodization through the step-like absorption feature. This mode of growth effectively prevents interparticle diffusion that could otherwise lead to the competitive growth of anisotropic $\beta\text{-AgI}$ nanocrystals. The absence of $\beta\text{-}$ or $\gamma\text{-CuI}$ in the optical spectra despite the large concentration of Cu reflects an efficient and rapid relaxation of the ‘amorphous’ Ag-I formed during the early stage of iodination into well-defined short-range order with Cu involved in a random manner. Thus, in the fully formed AgI films, Cu would reinforce the cation ‘sublattice’ and contribute to the mechanical strain that leads to confinement of excitons.

To further retard the iodization and to ensure better crystallite size distribution, Sb was used as a dopant for AgI. Such an additive modifies the thin film morphology; besides acting as nucleating centers leading to controlled Ag island formation in growing Ag-Sb alloy films [16]. Optical absorption and photoluminescence studies were performed (the latter as a function of Sb concentration and excitation wavelength across the band edge) on the $\text{Ag}_{1-x}\text{Sb}_x$ ($x = 0.01, 0.05$ and 0.13) alloy films characterized by XRD and SEM [16, 17]. Slower evolution of the exciton band and clear absence of quasi-free excitonic PL observed in (Ag, Cu)I thin films are the major results. Sb encourages nanoparticle formation in a reversible place exchange mechanism and promotes an interface mediated donor-acceptor photoluminescence (detailed figures are available in refs. [16,17]).

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PHOTOLUMINESCENCE STUDIES ON CdS NANOCCLUSERS FABRICATED IN LANGMUIR-BLODGETT FILMS

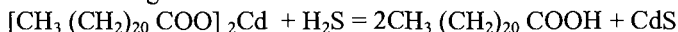
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In this paper we investigate photoluminescence (PL) of CdS nanoclusters fabricated in a Langmuir-Blodgett (LB) film matrix. The PL spectrum of the nanoclusters in the matrix comprises an asymmetrical band with a maximum at 2.4 eV. After removing the matrix the spectra consist of the high energy band at 2.9 eV and the two lower energy bands at 2.4 and 2.0 eV attributed to exciton recombination in nanoclusters, emission from defects in the LB matrix and surface states of nanoclusters, respectively.

Structures with CdS nanoclusters are promising candidates for of novel light-emitting devices. In the present work the photoluminescence (PL) of CdS nanoclusters in a Langmuir-Blodgett (LB) matrix of behenic acid and nanoclusters after removal of the matrix have been studied.

The films of cadmium behenate were formed by the LB method. A solution of cadmium behenate in chlorophorm was spread on water subphase to form monolayer of Cd salts. The films were transferred at room temperature onto silicon and quartz substrates at a surface pressure of 30 mN/m. The cadmium behenate films were exposed to H₂S gas at a pressure 100 Torr for 1–3 h at room temperature. As a result of the following chemical reaction



CdS nanoclusters within the behenic acid matrix were formed. The behenic acid matrix was removed in a hexane solution, or by thermal annealing in vacuum for 2 h at 200°C.

The samples were studied by room temperature UV-spectroscopy and PL. UV-VIS absorption spectra of films transferred onto quartz substrates were measured using a Shimatzu spectrophotometer. PL was excited using a pulsed N₂ laser (337 nm). The PL spectra of LB films on silicon su bstrates were registered using a monochromator equipped with photomultiplier operated in a photon counting mode.

Fig. 1 demonstrates the optical absorption spectra of LB films before and after the H₂S treatment. The absorption of the cadmium behenate film increases slowly with photon energy in the range 2.5–4.5 eV (curve 1). After the H₂S treatment an absorption edge is observed at 2.9 eV (curve 2). After a treatment in hexane the absorption edge does not change (curve 3). After annealing the edge shifts from 2.9 to 2.8 eV (curve 4). The observed shift of the absorption edge to higher energy with

respect to the bulk CdS bandgap (2.5 eV) is believed to be caused by size quantization of excitons in CdS nanoclusters. The size of semiconductor nanoclusters was estimated from the experimental data on exciton energy dependence on the cluster size. Using the data of Ref.1 the values of 2.5 and 3 nm were found for CdS mean cluster sizes in an LB film and after the annealing LB matrix, respectively.

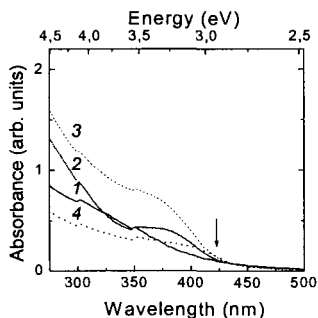


Figure 1. Optical absorption spectra of LB films of cadmium behenate: 1 – as-prepared film, 2 – the film after the H₂S treatment, 3 – the film after H₂S and hexane treatments, 4 – the film after H₂S treatment and annealing at 200°C. The arrow indicates the position of the absorption edge in curves 2–4.

Fig. 2(a) shows the PL spectra of LB films with different numbers of monolayers on silicon substrates. The spectrum of CdS nanoclusters in each LB film comprises an asymmetrical band with a full width at half maximum (FWHM) about 0.6 eV. The band maximum corresponds to the energy of 2.4 eV, which is less than the bulk CdS bandgap. The PL intensity increases with increasing the film thickness, the shape of the band remaining unaltered. In Fig. 2(a) the spectrum of an as-prepared cadmium behenate film is also shown. It is seen that there is no PL signal from cadmium behenate. In Fig. 2(b) the spectra of CdS nanoclusters in an LB matrix and after removing the matrix are compared. After removing the matrix the PL intensity decreases by more than 10 times. The PL spectrum of the sample after the hexane treatment consists of three bands at 2.9, 2.4 and 2.0 eV. After annealing the PL spectrum consists of the bands at 2.9 eV and 2.1 eV, which is well approximated by a sum of two bands: one at 2.4 eV and another at 2.0 eV. The curve 4 and the dotted lines in Fig. 2(b) show the deconvolution of the spectrum 1 (nanoclusters in a matrix) into three bands with their maxima at 2.9, 2.4 and 2.0 eV. The positions and widths of these bands are in a good agreement with those of the bands observed in the PL spectra of nanoclusters taken after removing the matrix.

We suggest that the high-energy PL band at 2.9 eV observed after removing the matrix corresponds to recombination of excitons in nanoclusters. The position of this band is in a good agreement with the mean nanocluster size estimated from the absorption spectra.

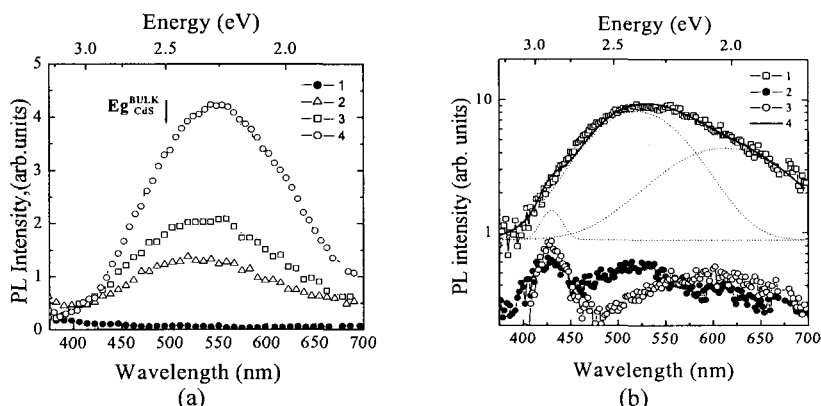


Figure 2. (a) PL spectra of LB films on silicon substrates before and after the H_2S treatment. 1 – as-prepared film of cadmium behenate; 2–4 – films containing 30, 40 and 80 monolayers of cadmium behenate, respectively, after the H_2S treatment. The arrow indicates the position of the bulk CdS bandgap. (b) PL spectra of CdS nanoclusters fabricated in an 80 monolayer LB matrix. 1 – nanoclusters in the matrix, 2 – nanoclusters after removing the matrix by hexane, 3 – nanoclusters after removing the matrix by thermal annealing, 4 – approximation of the spectrum 1 by three Gaussian curves shown by dotted lines.

We assume that the 2.4 eV band seen after removing the matrix by the hexane treatment corresponds to recombination involving defect states in the matrix. The optical absorption spectra indicate that the excitation laser radiation is absorbed in the residual matrix material, which was not removed during the treatment. In addition, the PL intensity of the 2.4 eV band is lower after annealing the sample, which indicates that a larger portion of the matrix is removed.

The band at 2.0 eV seen after removing the matrix is associated with the PL from surface states located at the nanocluster-matrix interface.

The asymmetric band at 2.4 eV observed in nanoclusters in the matrix composed of three bands can correspond to the following processes: exciton recombination in nanoclusters, PL from defects in the matrix, and PL from surface states of nanoclusters. A decrease of the PL intensity after removing matrix is explained in terms of reducing the numbers of defect states and surface states of nanoclusters.

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IMMUNOLABELING OF MEMBRANE PROTEINS AND CELLS BY HIGHLY FLUORESCENT CADMIUM SELENIDE NANOCRYSTALS

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We have prepared extremely bright bioconjugates of highly luminescent (CdSe)ZnS nanocrystals with antibodies and demonstrated their advantages in fluorescent immunolabeling of cancer cells. The improved stability of bioconjugates with nanocrystals was achieved by applying additional polyelectrolyte layer on the surface of nanocrystals. Much higher photostability of bioconjugates with nanocrystals, as compared with standard fluorescent dyes, allowed to proceed careful long-lasting 3D fluorescent imaging of p-glycoprotein, one of the principal mediators of multidrug resistance phenotype of cancer cells.

1 Introduction

Highly fluorescent core-shell II-VI nanocrystals are perspective materials in immunolabelling due to their narrow symmetric emission line (25-40 nm), the spectral position of emission controlled easily by the size of nanocrystals, single-source excitation of nanocrystals with different emission color [1,2] and high photostability (380-fold higher than commonly used dye AlexaFluor [3]). Nanocrystals (quantum dots, QDs) with CdSe core and ZnS shell synthesized by the high temperature reaction between organometallic precursors in highly coordinating solvents, like trioctylphosphine oxide (TOPO) and hexadecylamine (HDA), exhibit the photoluminescence (PL) quantum yield exceeding 60% at room temperature and

emission color varied from cyan (ca. $\lambda = 500$ nm) to red ($\lambda = 600\text{--}640$ nm) by changing the diameter of core from 2 to 6 nm [4]. Since, the routine synthesis produces hydrophobic QDs easily soluble in chloroform, hexane etc. but not in a water, an additional operation should be carried to convert QDs into water-soluble stuff. This operation is extremely important and all further biochemical properties of QDs fluorescent labels are sensitive to the parameters of this operation. The usual way to make water-soluble QDs is based on exchange of surface hydrophobic molecules (TOPO, HDA) onto hydrophilic mercaptanes, like mercaptoacetic acid, cysteine, cysteamine etc. Such molecules are bound chemically to the surface Zn atoms of the core-shell (CdSe)ZnS QDs via mercaptogroups, whereas carboxylic or aminogroups are suitable for further conjugation with biomolecules. In order to increase the stability of QDs against photocorrosion (photooxidation of --S-Zn bonds results in destroy of QDs solubilizing shell), we have deposited additional stabilizing poly(allylamine) layer on the surface of QDs before their conjugation. Conjugation of resulted solubilized QDs with the secondary antibodies (Abs) led to the product with extremely low non-specific binding to the cell surface, demonstrated high specificity of binding to anti-p-gp primary Abs in immunofluorescent dot-blot detection and 3D confocal localization of p-gp within the membrane of cancer cell.

2 Methods

(CdSe)ZnS core-shell QDs with 4 nm diameter CdSe core were synthesized accordingly [5]. The thickness of ZnS shell was about 1-2 nm. The solubilization of QDs in water was achieved by treating a colloidal solution of QDs in chloroform with DL-cysteine (Cys). After complete exchange of surface TOPO molecules onto Cys ones, QDs became no more soluble in hydrophobic chloroform and precipitated. The deposit was washed out of residuals and redissolved in water buffer (pH=8) under sonication providing an aqueous colloidal solution of QDs with bright orange PL and quantum yield about 40% at room temperature. Finally, QDs were covered with monolayer of poly(allylamine) via electrostatic interaction between carboxylic groups of Cys and aminogroups of poly(allylamine).

Poly(allylamine)-coated QDs were conjugated with anti-mouse polyvalent Abs using EDAC as a cross-linker [3]. The parental MCF7 (MCF7/WT) cells are issued from human breast adenocarcinoma cell line (ATCC). The multidrug resistant (MDR) subclone MCF7/ADR (MCF7r) was provided by Dr A. Trussardi. The cells were fixed first by 10% formol, pH 7.4 for 20 min at room temperature and then incubated with 5 $\mu\text{g/ml}$ of anti-p-gp primary Abs (Amersham) in blocking solution. After incubation for 90 min at room temperature, cells were washed with PBS containing 0.5% Tween and covered with 1:20 dilution of anti-mouse polyclonal Ab linked to QDs (Ab-QDs) in blocking solution or with 1:20 dilution of FITC-Ab conjugates (Dako) in blocking solution (FITC is the standard green fluorescent dye). The cells were incubated during 60 min at room temperature, washed three times

with PBS containing 0.5% Tween and analyzed using routine epifluorescence microscope for immunofluorescence detection of p-gp or studied with 3D confocal Bio-Rad fluorescent microscope for localization of this protein within the membrane of the cell.

3 Results and discussion

Extremely high photostability of QDs-Abs conjugates, as compared to FITC-Abs allow to use them for long-lasting 3D confocal analysis of p-gp distribution in the membranes of MCF7r cancer cells without any detectable lost of fluorescent signal. Fig. 1 shows 3D image reconstructed from 140 confocal fluorescent images of single MCF7r cell overexpressing p-gp. Each bright spot represents an emission from single QD-Ab. It should be pointed out, that 3D fluorescent immunoanalysis of single cells with standard FITC-Abs conjugates is impossible, since the time for collecting hundreds of confocal fluorescent images from the same cell is greatly exceeds the half-time of FITC-Abs photodegradation (about 0.4 min).

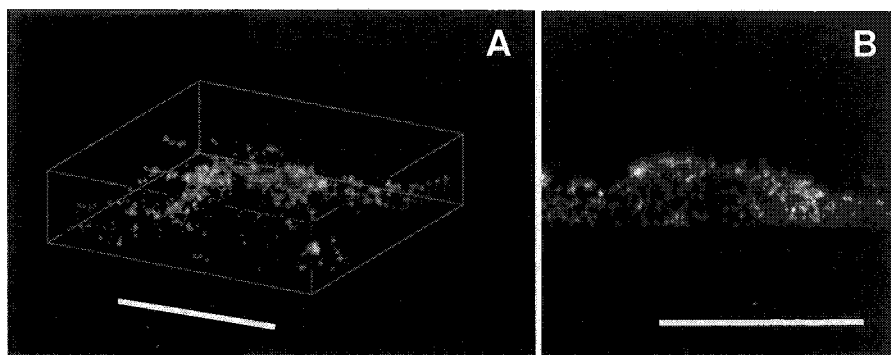


Figure 1. 3D image reconstructed from 140 confocal fluorescent images of single MCF7r cell overexpressing p-glycoprotein: A – top view, B – side view. Cells were incubated with primary anti-p-glycoprotein Abs, then further stained with secondary anti-mouse polyclonal Abs conjugated with fluorescent nanocrystals. All sections were recorded using 60 x magnification and zoom 3x. Scale bar is 4.5 μm.

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LUMINESCENT CODING BY QUANTUM DOTS: MICROCAPSULES LOADED WITH SEMICONDUCTOR NANOCRYSTALS

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Polymer microspheres (0.5-5.0 micron in diameter) coded either with a single luminescence color or with multiple colors of controlled emission intensity ratios have been fabricated by the charge-driven encapsulation of water-soluble CdTe nanocrystals luminescing in the visible and near IR. Thiol-capped CdTe nanocrystals used for encapsulation are stable against photobleaching and have narrow and symmetric emission peaks tunable with a particle size (2.0-6.0 nm) from green (510 nm) to the near IR (730 nm) with quantum yields of up to 40%. The encapsulation occurred by pumping of negatively charged nanocrystals into the interior of specially designed polymer spheres consisting of a polymer shell and a core containing the solution of a positively charged polyelectrolyte, or *vice versa*.

1 Introduction

The perspectives of deployment of semiconductor nanocrystals as fluorescence labeling reagents for biological imaging experiments have been demonstrated recently [1]. Semiconductor nanocrystals are photostable, and have nearly continuous excitation spectra above the threshold of absorption together with a strong, narrow and symmetric emission band which depends on the particle size. Therefore, many-color probes can be simultaneously excited by a single narrow-band excitation source and distinguished in a single exposure. Multicolor optical coding for biological assays has been also shown to be possible with polymer microspheres tagged with specific and identifiable combinations of differently-sized CdSe/ZnS nanocrystals [2]. The colored bar code generated on colloidal spheres can be easily decoded by fluorescence microscopy. Here we present a general concept of the charge-driven microencapsulation of luminescent nanocrystals in aqueous solutions [3].

2 Experimental

Thiol-capped CdTe nanocrystals used for encapsulation are stable against photobleaching and have narrow and symmetric emission peaks tunable with a particle size (2.0-6.0 nm) from green (510 nm) to the near IR (730 nm) with

quantum yields of up to 40%. The nanocrystals used in this work were stabilized either by thioglycolic acid or by 2-mercaptoethylamine, thus possessing either negative or positive surface charge.

The microcapsules used in this work were prepared by the recently developed approach of colloidal templating. It makes use of both the controlled precipitation and the layer-by-layer assembly of polyelectrolytes on colloidal polymer cores leading to the double shell structure. The core can be dissolved, and the inner shell decomposed releasing the polymer into the capsule interior. Thus, the liquid core contains either positively or negatively charged polyelectrolyte depending on the material of the inner shell. The outer polymer multilayer shell remains intact providing the capsule stability from one hand and the permeability for nanoparticles from the other hand. Encapsulation of CdTe nanocrystals in microspheres was achieved by soaking the latter in aqueous 0.2 M NaCl solution containing $\sim 10^{-3}$ M CdTe (referred to Te) for 1 h at neutral pH. Electrostatic forces move nanocrystals inside the polymer spheres containing oppositely charged polyelectrolyte. Once penetrated, the nanocrystals remain captured because of the electrostatic interactions between the oppositely charged groups of the stabilizer molecules and the polyelectrolyte molecules.

3 Results and discussion

CdTe nanocrystals of any available size and, thus, any emission color in the spectral region from green to the near IR can be encapsulated by the above described procedure, providing the single-color tagged microspheres (Fig. 1). Multicolor tagged microspheres were prepared by the same technique as it was used for the single-color samples by soaking the polymer capsules in aqueous dispersions containing mixtures of nanocrystals of different sizes. The simultaneous loading of up to 5 different sizes of CdTe nanocrystals has been done, providing microspheres appearing whitish-orange in the confocal microscope.

Fig. 2 shows the balanced luminescence spectra taken from the aqueous dispersions of two-color tagged spheres with 3 different ratios of the well-separated emission peaks. The relative amount of each kind of nanocrystals encapsulated depends on the number of particles in the solution, as it was proven by almost linear relationship between the luminescence intensity of a single color in the two-color tagged spheres and the concentration of the correspondent CdTe nanocrystals in solution. This allows the control of the relative emission intensity ratios at different wavelengths and can be used in addition to the luminescence color to create microspheres carrying unique multiplexed codes.

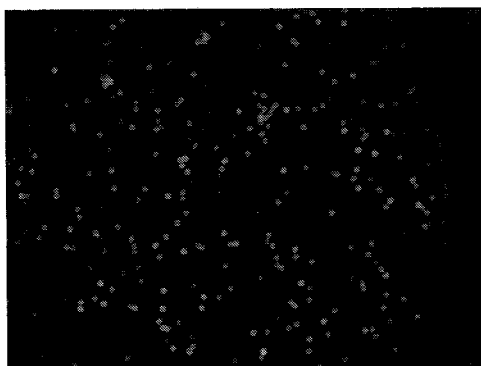


Figure 1. Fluorescence micrograph of a mixture of polymer spheres (5 micron in diameter) loaded with CdTe nanocrystals of different sizes.

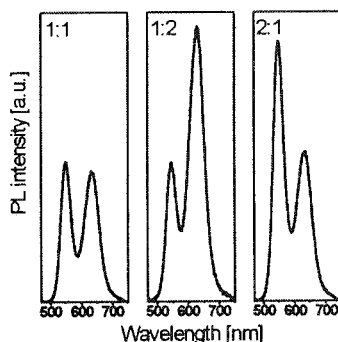


Figure 2. Luminescence spectra of two-color tagged microspheres showing two separate peaks with controlled intensity ratios.

4 Conclusion

In conclusion, polymer microspheres coded either with a single luminescence color or with multiple colors of controlled emission intensity ratios have been fabricated by the charge-driven encapsulation of water-soluble CdTe nanocrystals luminescing in the visible and near IR. The encapsulation occurred by pumping of negatively charged nanocrystals into the interior of specially designed polymer spheres consisting of a polymer shell and a core containing the solution of a positively charged polyelectrolyte, or *vice versa*. Color-tagged microspheres can be further used for multiplexed optical coding of biomolecules and biological cells, and for creation of encoding combinatorial libraries.

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IN VITRO BIOACTIVITY TESTING OF ZrO_2 NANOPOWDERS PREPARED BY MW-ASSISTED HYDROTHERMAL SYNTHESIS

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Zirconia nanopowders obtained by hydrothermal synthesis were tested *in vitro* at 60°C for 30 days. Elemental analysis, XRD, SEM, TEM, techniques were used for this study. Crystallinity and phase identification was performed before and after *in vitro* test.

1 Introduction

Recent advances in microwave technology have met the challenge of providing faster, cleaner, safer, more reproducible, and more accurate nanopowders preparation alternatives [1-3]. The combination of pressurized digestion with the precise heating control possible with microwaves was an instant success, in the field of analytical chemistry in the mid-1970s whilst in the late-80s it was extended to synthetic purposes. Precise feedback control of reaction parameters has been available for some time, and though it is better than ever, the digestion vessels themselves have provided the means to extend the instrument's capabilities into higher temperatures and pressures typical of hydrothermal synthesis. The microwave cavity is nowadays functionalized with an integrated infrared monitoring of all reaction vessels, multilayered door construction, "snap-in" sensor connections, corrosion-resistant coating of all metal surfaces. An advanced feedback power control has transformed the instrumentation into an easy-to-use automated system with a high sample throughput. Vessel design allows control of temperatures up to 300 °C and pressure up to 800 psi [4], and some continuous flow reactor are also available on the market.

The aim of this paper is to present the use of a microwave digester to prepare nanopowders via hydrothermal route. In the field of biomaterials the researchers (due to some problems with the traditional materials) are looking for the design of biomaterials with surface properties similar to physiological bone (grain sizes in the nanometric range [5]). This would aid in the formation of new bone at the tissue/biomaterial interface and therefore improve implant efficacy. With the advent of nanostructured materials (materials with grains sizes less than 100 nm in at least

one direction [6]) it may now be possible to prepare materials which simulate the surface properties of a physiological bone. The use of zirconia ceramics, with several advantages over other ceramic materials started about twenty years ago [7]. In this work we report the characterisation and the *in vitro* study of nanometric particles of ZrO_2 .

2 Sample preparation

Nanocrystalline ZrO_2 powders were prepared starting from $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (RPE, Carlo Erba, Milan, Italy) aqueous solution 0.5 M [8,9]. The solution was neutralized with NaOH 1 M to pH 10. Then 20 ml of the solution was poured in each of the five Teflon vessels of the microwave reactor. The reactions were conducted using a MW reactor (mod. MDS 200, CEM Corp.). The system operates at 2.45 GHz and the maximum power used was 450 W. The power level was automatically adjusted to the maximum pressure, which was 180 psi corresponding to a maximum temperature of 120°C. The reaction was completed after 2 h of the hydrothermal treatment and the solid phase was separated from the solution by filtering. The powders were washed free of salts with distilled water. One experimental run produced about 1.5 g of powder.

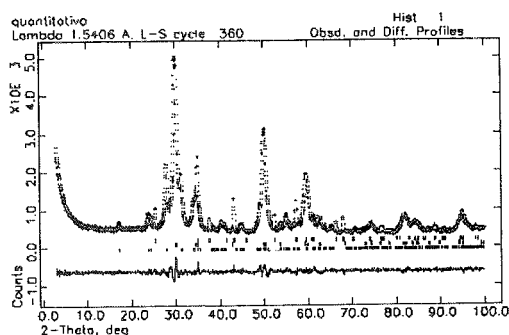
Crystalline phases were analyzed before and after *in vitro* tests with a powder diffractometer (PW3710 Philips) operating with the CuK_α radiation. The data were collected in the 2θ angular range 20-60° (2θ) (qualitative analysis) or 3-100° (2θ) (quantitative analysis). Interpretation of diffraction patterns involves measurement of diffraction spacings and comparison with known spacings of standards materials [10]. The quantitative X-ray diffraction (XRD) analysis was performed using the combined Rietveld and reference intensity ratio (RIR) methods [11-15] (by GSAS [16]). The average grain size was determined by means of the Scherrer's formula. Moreover, the nanopowders were investigated by means of transmission electron microscopy (TEM) (JEM 2010, JEOL). For the TEM studies the powders were dispersed in distilled water and a drop of suspension was placed on a copper grid with a transparent polymer and dried. Elemental analysis was performed by inductively coupled plasma (ICP) spectrometer, (Spectroflame Modula, Spectro). The *in vitro* test were performed leaving the nanopowders for 30 days in three different solutions: distilled water, SBF (simulated body fluid [17]) and SBF added of citric acid (0.08 M), at 60°C. This temperature was chosen to better evaluate the powder behaviour under the most extreme conditions.

3 Results and discussion

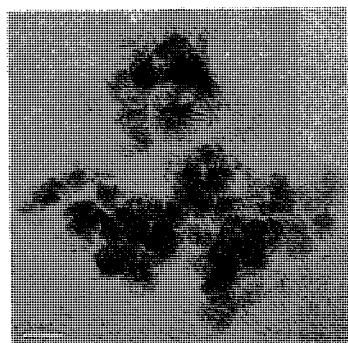
The X-ray diffraction analysis revealed the main phase to be ZrO_2 in the tetragonal and monoclinic forms. The results derived from quantitative analysis by Rietveld-RIR method indicate also the presence of amorphous phase (Figure 1a and Table 1).

Table 1. Quantitative XRD analysis of the ZrO_2 powders (wt.%)

Phase	ZrO_2
tetragonal	36 (1)
monoclinic	22 (1)
amorphous	42 (1)



(a)



(b)

Figure 1. (a) Quantitative analysis by Rietveld RIR method: (+) observed and calculated (-) patterns of the examined powders; (b) TEM micrograph of investigated powders before *in vitro* test.

TEM investigation reveals that the powders (Fig. 1b) are rather monodisperse with dimension in the range of 5-10 nm. Electron diffraction patterns show that the nanometric powders are composed of single crystals. The *in vitro* tests does not alter the dimension of the particles. Their reactivity (evaluated by the release of zirconium ion in the solution) is varying and in the subsequent order: SBF (with acid citric)>SBF> H_2O . These are also confirmed by the XRD: the peak intensity decreases in the same order, but their position is unchanged; there is no evidence of transformation of the tetragonal phase in the monoclinic, that could inhibit mechanical properties of the powder [7]. These agree with those obtained from the correspondent micrometric product [18]. In the present study the reactivity is greater, probably due to the different dimension of the particles.

Acknowledgements

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COPPER NANOPARTICLES WITHIN AMORPHOUS AND CRYSTALLINE DIELECTRIC MATRICES

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Two types of 'Cu-nanoparticles-in-dielectric' nanocomposites were produced through hydrogen reduction of Cu(II): Cu-zeolite and Cu-zeolite-silica. Amorphous silica was prepared by the sol-gel technique and served as optically transparent matrix incorporating zeolite microcrystals. The copper nanoparticles provide an optical response of the composite material due to the plasmon resonance band varied due to changes of matrix features.

1 Introduction

Metal nanoparticles as potential components of new generation electronic devices are of great interest due to promising features with explicit size-dependence of their physical properties. Electro- and photostimulated charge transfer processes in materials with nanoparticles are challenging for development of ultrafast switching elements. Many tasks in fabrication of devices with nanoparticles are the proper control of size, shape and position of nanoparticles providing desirable properties.

In the present work, we consider the two approaches for synthesis of nanoparticles designed for metal particles and being in the progress for ultrafine semiconductors. They allow to fabricate nanocomposites of the type 'nanoparticles-in-dielectrics' with amorphous and crystalline matrices. The first one is based on the sol-gel technique producing dielectric silica films with nanoparticles incorporated within silica matrix [1]. Nanoparticles provide an optical response of the material due to the plasmon resonance [2] with variable spectral position and band shape. In the second approach nanoparticles are produced within the crystalline zeolite matrices which stabilize both the few-atomic clusters (e.g., Ag₈) and metal particles in the size range of 1-20 nm [3]. Chemical routes of their synthesis admit easy control of size and optical properties. The metal nanoparticles in zeolites can be transformed into semiconductors without destroy of the zeolite matrix and with incorporation of zeolite microcrystals into transparent silica films. This construction

can be appropriate for design of optical elements. We have fabricated also hybrid samples with the metal particles incorporated within zeolite microcrystals those are immersed into the solid amorphous sol-gel matrix. Such nanocomposite allowed us to use features of ultrafine zeolite pores with molecular dimensions in the fabrication of transparent optical films.

2 Method

Fabrication of doped sol-gel silica films. Precursor solutions for sols were prepared by mixing tetraethoxysilane, ethanol and water with HCl as catalyst in the molar ratio 1:6:6:0.08, respectively. That is conventional procedure commonly used for silica sol-gel films preparation [4]. Cu-doped films were fabricated from the sols mixed with different amount (5-30 wt.%) of $\text{Cu}(\text{NO}_3)_2$ by means of spin-coating on a quartz substrate under the rotation speed 2000 rev/min. Films were heated at 500°C during 1 min in air. These films contain copper in the form of CuO that was established by the direct XRD analysis [5]. A heat treatment of the Cu-doped silica films in hydrogen atmosphere at 600°C for 1 h resulted in reduction of copper oxide to the finely dispersed metallic copper.

Preparation of zeolite samples. The H-form of mordenite (supplied by TOSOH Corporation, Japan) with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (MR) equal to 206 was used, however, the principles proposed here may be used for a broad class of metal ion-containing zeolites. This MR value means that the ion-exchange capacity of this zeolite was rather low. The ionic exchange was performed at room temperature in 0.1N $\text{Cu}(\text{NO}_3)_2$ aqueous solution for 24 h. Suspensions of Cu-mordenites obtained were filtered, washed and dried at 100°C for 2 h.

Cu-mordenite in silica sol-gel films. The fabrication procedure of Cu-mordenite-doped sol-gel films was modified as compared with the above Cu-doped ones by the change of copper nitrate onto Cu-mordenite. The subsequent deposition of the sol onto quartz substrate resulted in formation of thin films similar to simple Cu-doped ones. Amount of Cu-mordenite was adjusted for fabrication of the films with sufficient optical quality. The films were heated in air at 500°C followed by heating in hydrogen atmosphere at 150-450°C. The latter temperature variance determined different reduction of Cu-mordenite, and similarly different results were obtained with mordenite within the silica sol-gel matrix.

Optical absorbance of the opaque powder-like Cu-mordenite samples was recorded with a Cary-300 (Varian) device as diffuse reflectance spectra (DRS), and usual absorption spectra were measured for transparent sol-gel films containing Cu-mordenite with a Specord M40 spectrophotometer.

3 Results and discussion

Fig. 1a displays a series of absorption spectra for Cu-mordenites with different MR, and very pronounced effect of this parameter occurs upon the optical properties of the Cu-exchanged and reduced zeolites. The plasmon resonance peaked at 580 nm develops for the sample with the lower MR while practically no reduction of copper was observed at the highest MR. The intermediate case (MR = 30) shows the weaker plasmon resonance with the line shape strongly different from the peak for MR = 10 sample, and a large amount of unreduced copper is evidenced by the rise in the end of spectral range presented. It corresponds to the familiar absorption of Cu^{2+} ions in pseudo-octahedral position and appears also in the unreduced Cu-mordenite samples as well in the data presented here for Cu-mordenite with MR = 206. The latter fact means that in the case of this sample (the lowest acidity

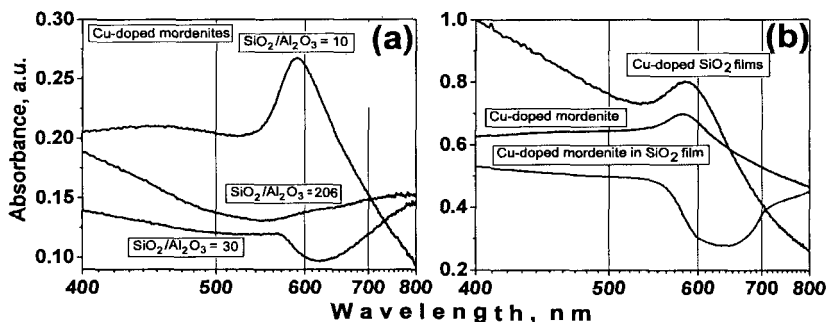


Figure 1. (a) Absorption (DRS) spectra of Cu-mordenites reduced under 250°C with different MR and (b) usual absorption spectra of the Cu-doped silica sol-gel films, of these films with Cu-mordenite with MR = 206 and the corresponding Cu-mordenite reduced under 450°C.

corresponds to it in the whole mordenite series with variable MR [6]) the reduction of Cu^{2+} is inhibited under this temperature. However, under the higher temperatures, 450°C, Cu-mordenite with MR = 206 can be effectively reduced (Fig. 1b), and the plasmon resonance band occurs similarly to that shown above for the lowest MR sample. Thus, Cu^{2+} states in mordenites with different MR can be transformed into fine copper particles responsible for appearance of the plasmon resonance band, and features of this band can be used for control of optical absorption of materials modified with metal-containing zeolites. We present here one version of such composite material in which Cu-mordenite with MR = 206 was incorporated into the sol-gel silica film (Fig. 1b). It should be noticed that copper reduced in the Cu-doped films develops also the plasmon resonance band similar with that in mordenites, and was observed also for copper nanoparticles produced in very different media: glasses, solutions, polymer films (e.g. [7]). The material fabricated from Cu-mordenite followed by the hydrogen reduction indicates also the plasmon resonance band from finely dispersed copper particles, however, its shape is like

with the reduced Cu-mordenite with MR = 30 rather than with the Cu-mordenite used for its fabrication (Fig. 1b). Theoretical evaluations made by us recently for these copper nanoparticles established correlation of the shape of this band with size of copper particles and dielectric function of a surrounding medium [6]. According to them, the intense plasmon resonance is generated by the particles of more size range (~10 nm for the band of the type given in Fig. 1a for MR = 10) than the particles with the step-like plasmon resonance band (e.g., the curve for MR = 30 in Fig. 1a). A value of dielectric function of the matrix also has the noticeable effect upon the shape of this band. These data allow us to suppose that copper nanoparticles formed in the mordenite matrix embedded into silica sol-gel film are of less size than the particles produced in this mordenite without the sol-gel film. This film can be an obstacle for efficient diffusion of Cu^{2+} -ions those are source of copper for the particle aggregation process. Amount of copper in this mordenite with MR = 206 is less than copper concentration within the Cu-doped films prepared by means of the direct Cu^{2+} introduction which resulted in the plasmon resonance with the pronounced maximum (Fig. 1b).

4 Conclusion

The two methods for synthesis of copper nanoparticles in dielectric matrices by the hydrogen reduction of copper ions are shown: within the Cu-doped silica sol-gel films and the hybrid Cu-zeolite-silica sol-gel optical materials on transparent substrate. Presence of zeolite microcrystals within sol-gel films gives more flexibility in variation of copper nanoparticle preparation. Optical features of copper nanoparticles in these systems are determined by their size and properties of surrounding medium and presented as the plasmon resonance band with different line profile.

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UV-VISIBLE CHARACTERIZATION OF GOLD CLUSTERS AND NANOPARTICLES IN BETA ZEOLITE

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The gold/zeolite system was prepared by ion exchange method. The gold introduced into Beta zeolite and reduced at various temperatures by hydrogen was studied by means of UV-Visible diffuse reflectance spectroscopy. Three types of gold species were observed in the samples: cations, clusters and nanoparticles.

1 Introduction

Gold deposited on metal oxides has been reported as active catalyst for many reactions [1]. Usually, gold exhibits activity when the size of its nanoparticles is less than 5 nm [2]. The stabilization of small metal particles and their activity strongly depend on preparation method and on support used [1]. Zeolite material possesses adjustable acidic properties and regular molecular-size channels in the crystalline lattice. These features provide inclusion of metal ions into zeolite matrix with subsequent transformation to ultrafine metal particles and clusters [3, 4]. In the present paper, the effect of changing of reduction temperature and concentration on the state of gold in Beta-zeolite were studied.

2 Experimental

A protonated form of Beta-zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to 20 was used for the sample preparation. The gold concentration in the samples was analyzed by energy dispersive spectroscopy. State of gold was studied by UV-visible diffuse reflectance spectroscopy. The spectra presented in Figs. 1,2 were obtained by subtraction of the support spectrum from the spectra of Au supported samples.

¹ On leave from Tomsk Polytechnic University (Tomsk, Russia).

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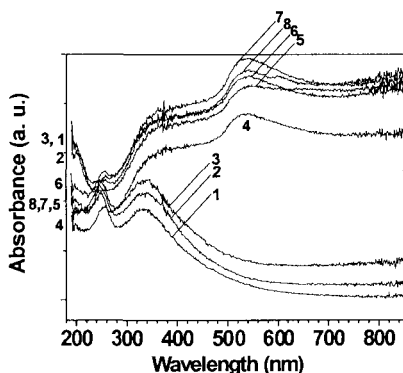


Figure 1. UV-Visible spectra of 1 wt.% Au/Beta before reduction (1) and reduced at: 25°C (2), 50°C (3), 100 °C (4), 200 °C (5), 300 °C (6), 400 °C (7), 500 °C (8).

The solution of $[\text{Au}(\text{NH}_3)_4](\text{NO}_3)_3$ complex of two different concentrations for ion exchange was prepared by reaction of HAuCl_4 with NH_4OH [5]. After ion exchange the samples were reduced by H_2 at different temperatures. The final concentrations of gold in the two samples measured by energy dispersive spectroscopy were approximately 0.5 and 1.5 wt. %.

3 Results and discussion

Several absorption bands of the ion exchanged form and reduced gold samples were detected with UV-Visible spectroscopy (Figs. 1,2). The band at $\lambda=190$ nm is attributed to the Au^{1+} ion according to reference data [6, 7]. The features at $\lambda=250$ nm and at 340 nm could be assigned to $\text{Au}_n^{\text{m}+}$ clusters [8]. The peak with maximum at $\lambda=550$ nm is assigned to the surface plasmon resonance of Au nanoparticles [6, 7] located on external surface of zeolite microcrystals. An increase of reduction temperature up to the 100°C (Figs. 1, 2) leads to the decrease of relative intensity of the peak associated with Au^{1+} and to rise of relative intensity of the plasmon resonance due to the nanoparticles. Further temperature increase does not reveal significant changes in the spectra.

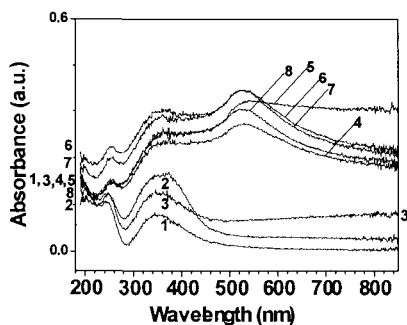


Figure 2. UV-Visible spectra of 0.5 wt.% Au/Beta before reduction (1) and reduced at: 25°C (2), 50°C(3), 100°C (4), 200°C (5), 300°C (6), 400°C (7), 500°C (8).

Spectra for the samples with different gold concentrations are similar except relative intensities, which rise with gold concentration. The sample with the lower concentration of gold shows higher contribution of gold species at 350 nm (which could be interpreted like clusters) than the samples with a higher concentration.

4 Conclusion

Gold clusters and nanoparticles were produced by means of the ion-exchange from aqueous solution followed by hydrogen reduction in the Beta-zeolite matrix. The method is similar to that for Ag; however, the complexation of Au precursor provides appearance of the cluster-like species at the ion exchange step. Au clusters and nanoparticles were detected by the optical features: the band of cations with the maximum in the range of 190 nm, clusters in the region of 280 and 340 nm and the plasmon resonance band in the region about 550 nm. The contribution of various Au species in the reduced samples can be regulated by concentration of gold in Beta-zeolite and reduction temperature. It is of interest for catalysis application.

Acknowledgements

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MANGANESE CARBONATE PARTICLES PREPARATION BY COLLOIDAL AGGREGATION FOR HOLLOW POLYELECTROLYTE CAPSULES FABRICATION

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Method for synthesis of monodisperse spherical-like manganese carbonate (MnCO_3) particles by colloidal aggregation process is developed. Hollow polyelectrolyte capsules have been prepared by means of layer-by-layer absorption of charged polyelectrolytes on microsized MnCO_3 particles with the subsequent decomposition of a micrometer nucleus. The use of inorganic templates is a way for clean capsules fabrication. The manganese carbonate particles and capsules obtained were investigated by SEM, SFM, XRD, and confocal fluorescent microscopy.

1 Introduction

In the last decade hollow spheres are extensively studied in the context of application as containers of prolonged action for substances of the different chemical nature: drugs, cosmetics, dye. A number of methods for preparation of microspheres with the sizes ranging from nanometers to micrometers and consisting of various materials are developed. Polyelectrolyte capsules have been produced by sequential adsorption of oppositely charged polyelectrolytes, also known as Layer-by-Layer (LbL) assembly onto the surface of colloidal particles followed by core dissolution [1-2]. Most of the capsules applications imply their chemical or physico-chemical modification by influence of the ionic strength [3], pH [3], temperature [4], polarity of solvent [5] on the morphology and physical properties of the wall, such as permeability.

In this paper, we present the data on the preparation of manganese carbonate spherical particles with different sizes which can be used as core for biocompatible capsules production.

2 Experimental

Materials. Sodium poly(styrenesulfonate) (PSS) MW 70000 and poly(allylamine hydrochloride) (PAH) MW 70000 were obtained from Aldrich. Ethanol, sodium

chloride, ammonium hydrogen carbonate, manganese (II) sulfate, were purchased from Sigma. All commercial materials were used without further purification. The water used in all experiments was prepared in a three stage Millipore Milli-Q Plus 185 purification system.

Confocal laser-scanning fluorescence microscopy (CLSM). The micrographs were obtained by means of a Leica confocal scanning system mounted to a Leica Aristoplan. A 100X oil immersion objective with the numerical aperture 1.4 was used. The standard filter settings for fluorescent excitation and emission were used.

Scanning electron microscopy (SEM). For SEM analysis the samples were sputtered with gold and measurements were conducted using a Gemini Leo 1550 instrument at an operation voltage of 3 keV.

Scanning force microscopy (SFM) images were obtained with a Digital Instruments Nanoscope IIIa in tapping mode.

3 Results and discussion

Formation of manganese carbonate spherical particles. Shape of particles is determined by the mechanism of their formation. Two main mechanisms of the particle formation are described in the literature: Ostwald ripening and particle growth by colloidal aggregation. Spherical particles are usually produced by colloidal aggregation. As was shown [6] manganese carbonate particles with spherical-like shape are immediately generated upon mixing manganese (II) salt and ammonium hydrogen carbonate solutions at the same concentration in the range of 1.6×10^{-2} - 1.6×10^{-1} mol/l at on-to on volume ratio in the temperature range 25-70°C. The formed particles showed a broad size distribution and average size varying in the range from 1 to 10 μm . For the preparation of monodispersed particles the most important requirement is the separation of nucleation and growth stage [7]. It is possible to do that in a poor solvent, for example ethanol.

Fig. 1 shows a general overview of the MnCO_3 particles synthesized when different ethanol quantity is added at vigorous agitation to solution of MnSO_4 (0.008 M) and NH_4HCO_3 (0.08 M). The average size and size distribution of MnCO_3 particles were affected by the ethanol concentration in the range from 0.1% to 5%. Average size decreased and size distribution was broader when the ethanol concentration was increased. The small crystals of MnCO_3 were prepared on the first stage of the process and then aggregated in secondary spherical particles. Ethanol influences on the primary particle formation and affects particles average size and size distribution.

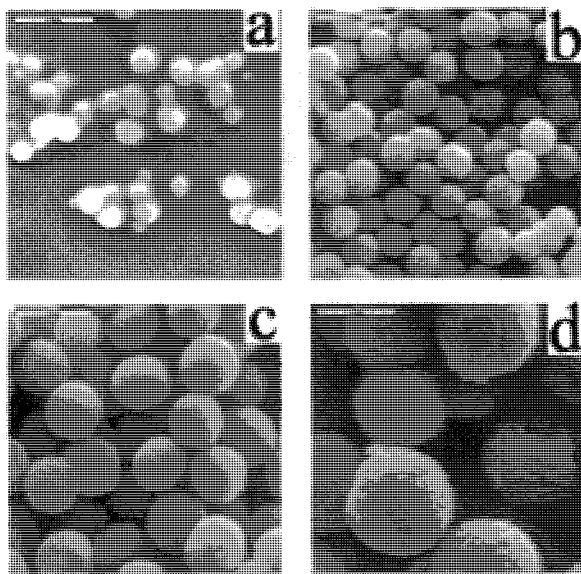


Figure 1. SEM images of MnCO_3 particles prepared from a solution of MnSO_4 (0.008 M) and NH_4HCO_3 (0.08 M) depending on concentration of ethanol a) 1.75%, b) 1.25%, c) 0.75%, d) 0.25%. Scalebar is 5 μm .

The influence of concentration of manganese (II) sulfate was studied in the range from 10^{-3} to 10^{-1} mol/l at fixed concentration ratio of $[\text{CO}_3^{2-}]/[\text{Mn}^{2+}] = 10$ and concentration ratios $[\text{CO}_3^{2-}]/[\text{Mn}^{2+}]$ in the range from 1 to 10 at constant concentration of manganese (II) sulfate (0.08 Ml). It was shown that at a low concentration of manganese sulfate or $[\text{CO}_3^{2-}]/[\text{Mn}^{2+}]$ concentration ratio manganese carbonate particles formed have non-spherical shape. Spherical particles of manganese carbonate were prepared only by colloidal aggregation procedure. Formation of the spherical particles by colloidal aggregation mechanism proceeds at concentrations of manganese sulfate higher than 0.004 M and concentration ratio $[\text{CO}_3^{2-}]/[\text{Mn}^{2+}] \geq 10$.

Hollow polyelectrolyte capsules were prepared as described earlier [8]. Monodisperse manganese carbonate particles with average size of 3.7 μm were used. We used the self-assembly method to prepare $(\text{PSS}/\text{PAH})_4$ hollow capsules.

After assembling of PSS and PAH multilayers the core can be dissolved at the conditions where the multilayers are stable, for example in acetic buffer at pH 3.0 during 24 hours. Fig. 2 shows a confocal and SEM images of the capsules prepared on the MnCO_3 template. The surface of the capsules clearly resembles the shape and the surface morphology of the cores used. From the AFM image it was also deduced that the thickness of the polyelectrolyte film is of the order of 20 nm for the 8-layers film. It is in good agreement with single polyelectrolyte layer thickness obtained for PSS/PAH capsules prepared on different templates.

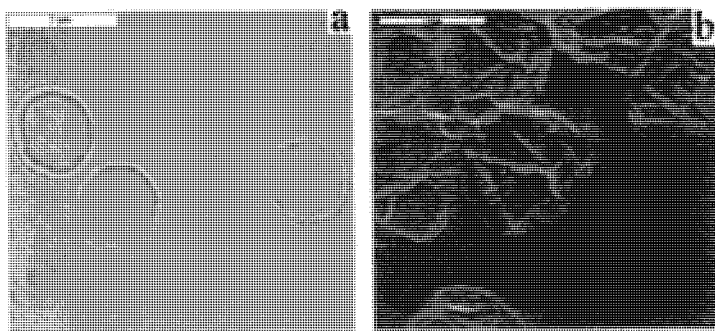


Figure 2. Confocal microscopy and SEM images of hollow polyelectrolyte capsules prepared by layer-by-layer on manganese carbonate particles. Scalebar is 5 μm .

Acknowledgements

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IMPURITY MOLECULE TRAPPING IN GROWTH OF NANOPARTICLES BY DEPOSITION FROM GAS PHASE

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Trapping of impurity molecules by nanoparticles growing by condensation from a gas phase is considered. The equation for the trapping coefficient is obtained. The dependence of the trapping coefficient on the system parameters is analyzed.

1 Introduction

The problem of impurity trapping in growing nanoparticles during their formation in a deposition from the gas phase is of interest for both different kinds of atmospheric processes and processes of modern technology (e.g., manufacture of nanoparticles). It is well known that even a very small concentration of impurity molecules in a condensed phase can substantially change certain physicochemical properties of the product. The control of the concentration of impurity molecules in the substance is of paramount significance in the production of microelectronics elements.

It should be noted that deposition processes in manufacture of nanoparticles often take place in a regime very far from equilibrium conditions [1]. The model for description of the impurity molecule trapping by growing nanoparticles should be valid for high non-equilibrium conditions. It should also describe the deposition process for arbitrary relation between the mean free path of gas molecules and the particle radius and take into account the trapping of non-condensable molecules. It is known that the gas-to-particle conversion can be realized by ordinary condensation (physical deposition) and by chemical deposition. Further we will consider the trapping of molecules by a small aerosol particle in physical deposition.

2 Results and discussion

It is known that an exact description of transfer processes in the aerosol particles-gas phase system with chemical or phase transformations on the particle surface for arbitrary particle sizes (and correspondingly for arbitrary Knudsen numbers) can be found only by solving the Boltzmann kinetic equation. However, the mathematical difficulties associated with the solution of the given equation lead to the necessity of obtaining rather simple expressions for mass and energy fluxes either on the basis of an approximate solution of the Boltzmann equation or with the use of simpler models. In particular, it is known that the use of the diffusion equation with appropriate boundary conditions on the particle surface leads to the equation that gives correct limiting cases with respect to the Knudsen number [2].

We assume further that the concentrations of vapor and impurity molecules are small in comparison with the concentration of a neutral buffer gas and use the diffusion equation to describe the mass transfer to the particles. The deposition problem is considered within the quasi-stationary approximation. For simplicity we assume the gas-particle system to be isothermal. The conditions on the particle surface and at the infinity distance from the particle can be written as

$$D_i \left. \frac{dn_i}{dr} \right|_{r=R} = J_i, \quad n_i|_{r=\infty} = n_{i\infty}, \quad (1)$$

where n_i is the number density of depositing molecules of the component i (further we mark the parameters of vapor by index 1 and the parameters of the impurity component by index 2), $n_{i\infty}$ is the number density of molecules of the component i at the infinite distance from the particle, D_i is the diffusion coefficient for the molecules of the component i , R is the particle radius, r is the radial coordinate from the particle centre, J_i is the resultant flux density of molecules of the component i into the particle. We assume further that the incident molecules are characterized by the Maxwell velocity distribution function.

The resultant flux density of the impurity molecules into the condensed phase is given by [3]

$$J_2 = \beta N_{2s} - \frac{J_2}{J_1 + J_2} F. \quad (2)$$

Here β is the sticking coefficient of impurity molecules, N_{2s} is the flux density of impurity molecules incident on the particle surface; the term F that characterizes the reevaporation of impurity molecules from the particle can be written in the form

$$F = n_c \left(\frac{kT}{2\pi m} \right)^{1/2} \exp \left\{ -\frac{Q}{kT} \right\}, \quad (3)$$

where n_c is the number density of the molecules in the condensed phase (it is assumed to be constant), k is the Boltzmann constant, m is the mass of the impurity molecule, Q is the evaporation energy of impurity molecules, T is the temperature.

Taking into account equations (1) and (2), in the case of $J_2 \ll J_1$ we can obtain the expression for the trapping coefficient of impurity molecules by growing aerosol particle G_p

$$G_p = J_2 \left(\frac{n_{2\infty} v_2}{4} \right)^{-1} = \frac{\beta}{1 + \frac{4F}{\alpha n_{1\infty} v_1} \left(1 + \frac{3\alpha R}{4\lambda_1} \right) \left(1 - \frac{n_{1e}}{n_{1\infty}} \exp \left\{ \frac{2\sigma V_m}{RkT} \right\} \right)^{-1} + \frac{3\beta R}{4\lambda_2}}, \quad (4)$$

where v_i is the mean velocity of molecules of the component i , n_{1e} is the number density of the saturation vapor, σ is the surface tension, V_m is the volume per molecule in a particle, λ_i is the mean free path of molecules of the component i ($i = 1, 2$), α is the condensation coefficient of vapor molecules (in derivation of equation (4) the condensation coefficient is assumed for simplicity to be equal to the evaporation coefficient).

It is seen from equation (4) that the value of G_p and hence the resultant flux of impurity molecules into the particle is greater than zero if $\beta > 0$ and the resultant flux of vapor molecules into the particle takes place. As follows from equation (4) the value of G_p decreases with a decrease of the Knudsen numbers Kn_i

($Kn_i = \frac{\lambda_i}{R}$) and increase of the parameter $\varphi = \frac{F}{n_{1\infty} v_1}$. The value of G_p can change under the influence of a resonance (e.g., laser) radiation [3]. It is related to a change of the values of α , β and Q in the resonance radiation field.

It should be noted that for rather small particles the values of the condensation coefficient of vapor molecules and the sticking coefficient of impurity molecules depend on the particle radius [4].

3 Conclusion

The equation for the trapping coefficient of impurity molecules by growing nanoparticles taking into account the dependence on Knudsen numbers for

condensing and impurity components and parameters characterizing the interaction of gas molecules with the particle surface has been obtained. It is shown that the trapping coefficient of impurity molecules (including a non-condensable component) is not equal to zero when the resultant flux of vapor molecules and sticking coefficient of impurity molecules are not equal to zero. The maximum value of the trapping coefficient takes place in free molecular region when $Kn_i \gg 1$.

Acknowledgements

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FORMATION OF NANOPORES AND COAGULATION OF NANOGRAINS IN CEMENTED TIN FILMS

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It is shown that the reaction of tin cementation onto zinc is reversible. Zinc ions in the solution affect the rate of tin deposition and tin film microstructure. The repeated processes of tin/zinc dissolution/deposition provide fabrication of rather thick films (2-5 μm), facilitate grain recrystallization and are responsible for the formation of narrow deep channels with a width not more than 30-50 nm.

1 Introduction

Cementation from aqueous solutions is widely used for metal coatings and powders production. It is the foundation of hydrometallurgical methods used for metal regeneration and purification of wastewaters.

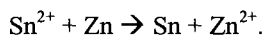
The cementation reaction is the electrochemical process in which metal ions from a solution are precipitated onto surface of a more electronegative metal. The process of cathodic deposition is coupled with the anodic dissolution of the substrate metal. The difficulty in ion diffusion through pores of the growing coating is the factor that limits the film thickness. As a rule, this thickness does not exceed 0.1-0.5 μm . More rare cases of dense film formation with a thickness of about several micrometers and with good adhesion to the substrate cannot be described by the suggested scheme.

The purpose of this work was to reveal the possibility and elucidate the mechanism of rather thick (2-5 μm) nanoporous tin film formation on zinc with the reverse cementation process.

2 Experimental

Tin films were deposited onto the fine grained underlayer of electrochemical zinc from solution 1 containing tin sulphate and sodium citrate (0.1 and 0.3 mol/l) and solutions 2 and 3 analogous to the first one but containing zinc sulphate (0.1 and 0.01 mol/l). Zinc sulphate was added to study its effect on the plating rate and tin film structure. The time-dependence of concentration of Sn^{2+} and Zn^{2+} ions was studied by atomic absorption spectroscopy. The microstructure and composition of

the surface was analyzed by SEM, TEM and XPS. The film thickness was determined by the gravimetric measurements assuming the reaction:



3 Results and discussion

It is determined that tin deposition from solutions on bright zinc substrates results in semiglossy coherent and uniform films. The growth proceeds for 3-5 hours and more with formation of tin films of 2-5 μm in thickness.

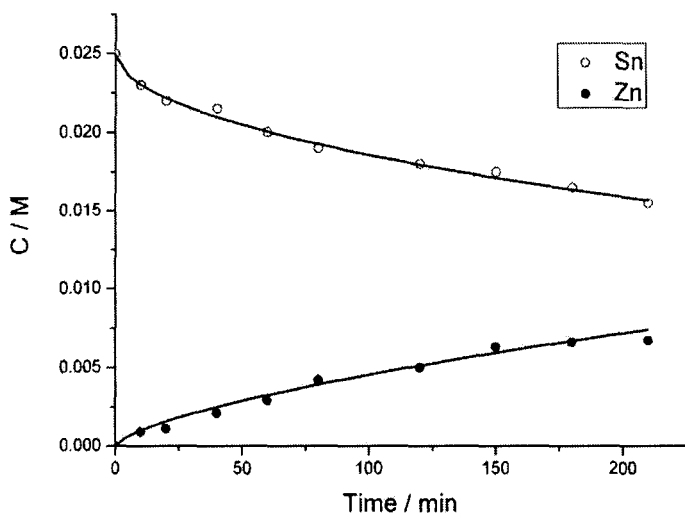


Figure 1. The time-dependence of Sn^{2+} and Zn^{2+} concentration during tin cementation onto zinc. Experimental conditions: 0.1 M SnSO_4 , 0.3 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$, 20°C.

Fig. 1 illustrates the changes in tin zinc ion concentration during the film growth. Taking into account the film compact microstructure and its thickness (up to ten microns) it is difficult to understand why the film growth is not interrupted by diffusion typical for cementation processes. Moreover, the addition of zinc ions into the solution (up to 0.01 M, solution 3) provides the increase in tin plating rate, but at the higher zinc ion concentration (up to 0.1 M, solution 2) the rate of film growth only slightly exceeds the rate of deposition from solution 1.

These observations can be explained on the basis of film composition data. So, earlier we had established [1] by means of Auger spectroscopy together with the ion etching of tin films cemented on zinc that the films under investigation at any stage

of their growth include 1-5 at.% of zinc in the bulk areas and 10-50 at.% in the near-surface layer (0.2 μm in depth).

Taking into consideration these data on zinc distribution we can propose the mechanism with zinc codeposition in the process of the tin reduction. It can be confirmed by the calculation of redox tin and zinc potentials with obstacles in mass transfer and real ion concentrations in the solution and near the growing surface.

The addition of zinc ions (0.01M) into the tin cementation solution provides close redox potentials of zinc and tin. As a result, conditions for zinc codeposition and the formation of microanodes can be attained not only on the substrate surface but also on the surface of growing grains. So, the diffusion process in ion transfer retardation through electrolyte to/from the zinc substrate between the growing grains is diminished.

It is necessary to note that the abundance of zinc ions in the electrolyte (0.1M) only slightly affects the deposition rate. It seems possible to explain this fact by competition of the two factors: zinc codeposition (positive) and mass transfer retardation due to evacuation of zinc ions from microanodes (negative). It allows us to conclude that the processes of tin and zinc reduction and dissolution are repeated many times while the tin film is growing. Such peculiarity of tin cementation in zinc has the principal effect on the nuclei growth and coalescence and, consequently, on film microstructure.

TEM results give evidence that the intensive formation of primary nuclei of 4-10 nm in diameter proceeds at the first stages of tin film deposition. Even a small increase in nuclei sizes up to 10-20 nm results in the formation of compact aggregates of 100-150 nm in diameter.

The further transformations of the film grains were studied by SEM (Fig. 2,3). The coalescence of nuclei in these aggregates leads to the formation of secondary microstructure represented by micro crystals (grains) with pores and channels between them. As a result of intensive new nuclei formation the grains are growing together, and new recrystallization proceeds with formation of conglomerates and crystallites about 1-3 μm in diameter. Narrow and deep channels with a width not more than 30-50 nm surround these crystallites. The new grains on the crystallite surface are isolated from these channels so that their growth cannot be provided by the zinc substrate.

Introduction of zinc ions into the tin cementation solution results in much more intensive grain coalescence and recrystallization and earlier appearance of crystallites (Fig. 3). These observations make clear the role of codeposited zinc nanoparticles in tin cementation and film growth.

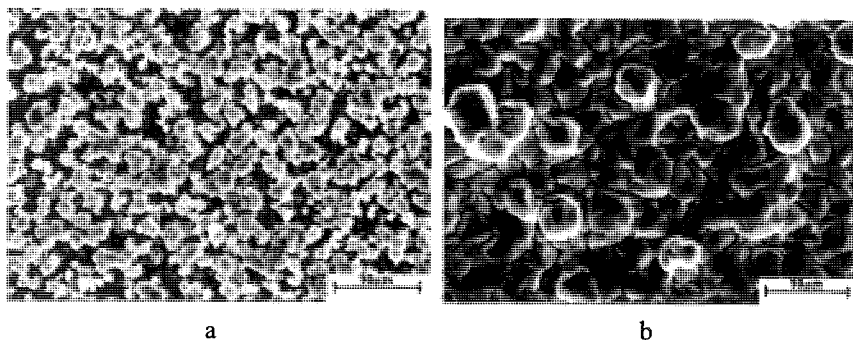


Figure 2. SEM images of tin deposits on zinc obtained by cementation reaction from solution 1 after a) 1 min, b) 20 min.

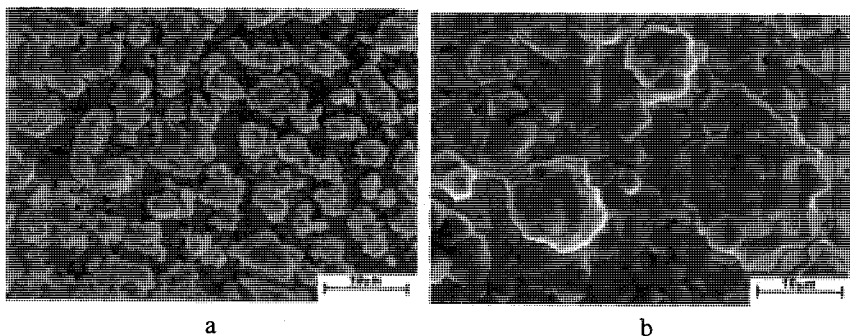


Figure 3. SEM images of tin deposits on zinc obtained by cementation reaction from solution 2 after a) 1 min, b) 20 min.

4 Conclusion

The reaction of tin cementation on zinc is reversible. The codeposited zinc reduces again tin ions from the solution. Tin films are formed with thickness of about 2-4 μm and more. The films include zinc in the near substrate zone (up to 10-50 at.%). These repeated processes of dissolution-deposition provide the low temperature recrystallization of the primary nuclei into grains and the grains into secondary agglomerates or crystallites of about 2 μm . The latter are separated by narrow and deep channels with the width not more than 30-50 nm.

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COMPARATIVE DFT CALCULATIONS OF SILVER CLUSTERS

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On the basis of systematical comparative DFT investigations of silver clusters, a novel functional has been developed the use of which provides the results close to the experimental data. Structures of anions Ag_7^- , Ag_9^- and Ag_{10}^- have been reliably identified for the first time.

1 Introduction

In spite of great interest in preparation and studying of silver clusters Ag_n , their structures are not clearly determined yet. Thus, only structures of clusters with $n=3,4,5$ are fairly well established. The most effective method of investigations of clusters structures is a comparison of quantum chemical predictions for different stable geometries with experimental data. The central problem in reliable identification of clusters structures by this method is an increase of the amount of structures characterized by closely allied values of energetic characteristics as the size of the cluster grows. As a consequence, structural assignment even for relatively simple clusters is a very difficult problem [1].

Here, we report on the elaboration of original functional the use of which with moderate basis set provides sufficiently high accuracy of calculations of different characteristics of silver clusters and on the reliable identification of structures of anions Ag_7^- , Ag_9^- and Ag_{10}^- .

2 Calculations of characteristics of silver clusters using the novel functional

2.1 Characteristics of silver clusters with $n \leq 6$

A comparative analysis of data on bond lengths (r_e), vertical detachment energies (VDE), excitation energies of neutral clusters with geometry of anions (T_e) and vertical ionization potentials of neutral clusters (IP_v) obtained by calculations within Density Functional Theory (DFT) [2] using SVWN, SVWN5, BLYP, G96LYP, B3LYP, B3PW91, B3P86 exchange-correlation functionals with LANL2DZ, SDD и DZVP basis sets for silver clusters with $n \leq 6$ have been carried out. It was found, that as a whole DFT methods provide a good agreement between the calculated and the experimental data for the mentioned characteristics. The selection of the functional is the determining factor whereas the used basis set does

not sufficiently influence the dependence of r_e , VDE, T_e и IP_v on the cluster size. However, the considered methods are beyond the capability of correct prediction of all considered characteristics simultaneously. This makes the identification of clusters structures difficult. Based on the performed analysis, we have build up some combinations of exchange and correlation functionals in such a way that their use with moderate basis set LANL2DZ [3] should provide sufficiently high accuracy of calculations of different characteristics of silver clusters. As a result, the following functional (XC) has been elaborated:

$$\alpha \cdot E_x^{LDA} + (1-\alpha) \cdot E_x^{HF} + \beta \cdot E_c^{LYP} + (1-\beta) \cdot E_c^{LDA},$$

where $\alpha = 0.7$; $\beta = 0.6$; E_x^{LDA} , E_x^{HF} , E_c^{LYP} и E_c^{LDA} are the designations of members showing exchange and correlation energies [2].

The calculated structures of silver clusters are shown in Fig. 1 and the data on VDE, T_e and IP_v values are presented in Table 1.

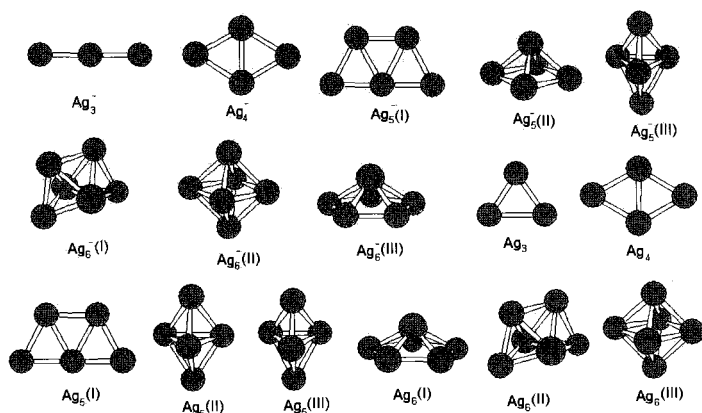


Figure 1. Optimized geometries of silver clusters.

As evident from Table 1, the difference between the calculated and the experimental values of VDE and T_e for the most stable isomers of anionic silver clusters does not exceed 0.1 eV. In the case of neutral clusters, the best agreement between the theoretical and the experimental IP_v values is also observed for the most stable isomers.

Table 1. Comparison of calculated and experimental characteristics of silver clusters.

Parameter	Ag ₂ ⁻	Ag ₃ ⁻	Ag ₄ ⁻	Ag ₅ ⁻ (I)	Ag ₅ ⁻ (II)	Ag ₅ ⁻ (III)	Ag ₆ ⁻ (I)	Ag ₆ ⁻ (II)	Ag ₆ ⁻ (III)
Experiment [1]									
VDE	1.1	2.40	1.63	2.12	-	-	2.08	-	-
T _(e)	1.7	1.19	0.77	1.20	-	-	0.28	-	-
Calculations									
ΔE	-	-	-	0.00	0.44	0.73	0.00	0.12	0.26
VDE	1.06	2.34	1.73	2.10	2.35	1.98	2.17	2.60	1.58
T _(e)	1.76	1.25	0.71	1.29	3.23	0.56	0.23	0.11	1.55
Parameter	Ag ₂	Ag ₃	Ag ₄	Ag ₅ (I)	Ag ₅ (II)	Ag ₅ (III)	Ag ₆ (I)	Ag ₆ (II)	Ag ₆ (III)
Experiment [4]									
IP _v	7.60	6.20	6.65	6.35	-	-	7.15	-	-
Calculations									
ΔE	-	-	-	0.00	0.44	0.45	0.00	0.36	0.73
IP _v	7.97	5.90	6.63	6.31	6.14	6.06	7.05	6.30	6.72

2.2 Identification of Ag₇⁻, Ag₉⁻ and Ag₁₀⁻ structures

Using the developed method we made a structural assignment of clusters Ag₇⁻, Ag₉⁻ and Ag₁₀⁻. Earlier, the discrepancy between theoretical considerations and experimental data for Ag₇⁻ and Ag₉⁻ has been observed, whereas the detailed study of Ag₁₀⁻ structure has not been carried out until now. The assignment has been based on both relative energy calculations and comparison of experimental and calculated photoelectron spectra (PES). The geometrical and energetic characteristics of seven isomers have been calculated for clusters of each size. For Ag₉⁻ clusters we did calculations of structures already reported in literature and some additional ones. The initial structures of Ag₇⁻ and Ag₁₀⁻ for geometry optimization were produced by capping energetically low lying Ag₆⁻ and Ag₉⁻ structures. The structures and relative energies of the most stable isomers are given in Fig. 2. The calculated and the experimental PES for these structures are presented in Fig. 3.

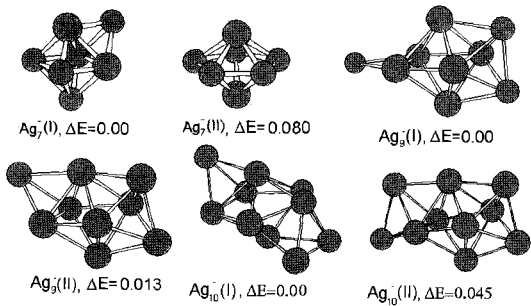


Figure 2. Optimized geometries and relative energies of silver clusters.

Fig. 3 shows that positions of PES lines calculated for $\text{Ag}_7^-(\text{I})$ and $\text{Ag}_{10}^-(\text{I})$ clusters are in a good agreement with the experimental data. The occurrence of two closely-spaced lines in the experimental PES of Ag_7^- is explained by splitting of the

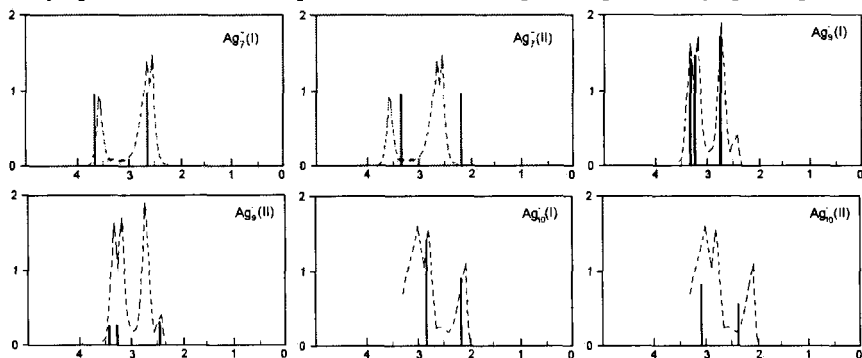


Figure 3. Experimental (dashed line) and calculated PES of silver clusters.

degenerate ^2E state. At the same time, for $\text{Ag}_7^-(\text{II})$ and $\text{Ag}_{10}^-(\text{II})$ clusters, a considerable discrepancy between the theoretical considerations and the experimental data is observed. Taking into account the fact that $\text{Ag}_7^-(\text{I})$ and $\text{Ag}_{10}^-(\text{I})$ have global minima on the potential energy surface, one can conclude that $\text{Ag}_7^-(\text{I})$ and $\text{Ag}_{10}^-(\text{I})$ correspond to structures which are observed in the experimental PES. According to the calculations, two structures make a contribution into the experimental PES of Ag_9^- cluster anion, namely, $\text{Ag}_9^-(\text{I})$ and $\text{Ag}_9^-(\text{II})$, more intense lines in spectra correspond to $\text{Ag}_9^-(\text{I})$ structure. This conclusion is in agreement with the data of calculations of relative energies of these structures.

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DFT CALCULATIONS OF COPPER CLUSTERS

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An investigation of spatial structure and energetic characteristics of copper clusters Cu_n with $n \leq 10$ have been carried out within the DFT model using the elaborated earlier functional XC. The structures of anions Cu_9^- and Cu_{10}^- have been identified for the first time.

1 Introduction

Recent years there have been a considerable interest in studying of binary catalytic systems based on stabilized nanocomposites and amorphous alloys of copper with other metals. The reason is that the catalytic activity of such systems in many cases is sufficiently higher than that of individual metals. The most convenient model for theoretical description of binary systems characterized by the absence of far order is a cluster model. However, quantum-chemical study of binary clusters comprises the significantly more complicated problem than that of individual metals, because a correct theoretical description of metal-another metal cluster systems requires that the used method should be in a position to provide good results of calculations of geometrical, electron structures and energetic characteristics of both of individual metals.

Earlier, a novel functional XC has been elaborated by us within Density Functional Theory (DFT), the use of which with LANL2DZ basis set provides sufficiently high accuracy of calculations of different characteristics of silver clusters [1]. In the present paper, a systematical study of copper clusters Cu_n with $n \leq 10$ has been carried out using the XC functional. With the aim of evaluation of the possibility of employment of this method for calculations of binary silver-copper clusters, the accuracy of the obtained data has been compared with the corresponding data for silver clusters.

2 Calculations of characteristics of copper clusters

2.1 Characteristics of copper clusters with $n \leq 7$

At the first stage, the calculations of bond lengths (r_e), vertical detachment energies (VDE), excitation energies of neutral clusters with geometry of anions (T_e) and vertical ionization potentials of neutral clusters (IP_v) have been performed for

copper clusters with $n \leq 7$ using the XC functional with LANL2DZ [2] and SDD [3] basis sets.

The calculated structures of copper clusters are shown in Fig. 1 and values of VDE, T_e and IP_v are presented in Table 1.

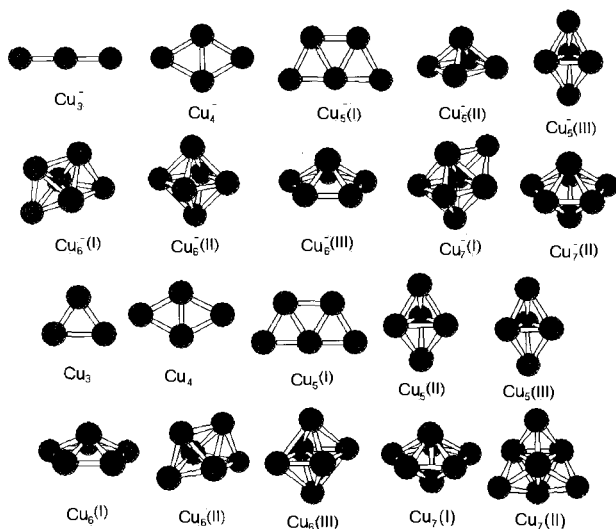


Figure 1. Optimized geometries of copper clusters.

As evident from Table 1, a good agreement between the calculated and the experimental data on VDE and T_e is observed for the most stable isomers. The calculations using SDD basis set provide somewhat closer correspondence between the experimental and the theoretical data than in the case of LANL2DZ basis set. The difference between the calculated and the experimental values of VDE and T_e for XC/SDD does not exceed 0.15 eV. The predicted values of IP_v for neutral clusters are also in a good agreement with the experimental data.

It was found that neutral and anionic clusters of copper and silver are characterized by closely allied values of relative energies of ground states as well as by very similar structures. The distinctions are observed in the case of anionic heptamers only. According to the calculations, more intense lines in the photoelectron spectra (PES) correspond to the $Cu_7(I)$ structure (Fig. 2).

Table 1. Calculated and experimental characteristics of copper clusters.

Parameter	Cu ₂ ⁻	Cu ₃ ⁻	Cu ₄ ⁻	Cu ₅ (I)	Cu ₅ (II)	Cu ₅ (III)	Cu ₆ (I)	Cu ₆ (II)	Cu ₆ (III)	Cu ₇ (I)	Cu ₇ (II)
Experimental data [4]											
VDE	088	24	145	197	-	-	20	-		24-26	-
T _(e)	20	1.1	0.8	1.2			03	-		075-095	-
XC/LANL2DZ											
ΔE	-	-	-	0.00	0.30	0.56	0.00	0.03	0.40	0.00	0.028
VDE	070	204	143	181	341	1.69	1.98	2.43	1.39	2.48	2.03
T _(e)	203	135	077	137	3.68	0.71	0.23	0.003	1.53	0.99	1.13
XC/SDD											
ΔE	-	-	-	0.00	0.29	0.56	0.00	0.06	0.46	0.00	0.025
VDE	092	232	157	197	2.25	1.74	2.07	2.60	1.47	2.57	2.09
T _(e)	201	1.16	0.78	1.34	1.80	0.82	0.24	0.04	1.54	0.96	1.15
Parameter	Cu ₂ ⁻	Cu ₃ ⁻	Cu ₄ ⁻	Cu ₅ (I)	Cu ₅ (II)	Cu ₅ (III)	Cu ₆ (I)	Cu ₆ (II)	Cu ₆ (III)	Cu ₇ (I)	Cu ₇ (II)
Experimental data [5]											
IP _v	79	614±1	70	630	-	-	-	-	-	-	-
XC/LANL2DZ											
ΔE	-	-	-	0.00	0.31	0.33	0.00	0.23	0.47	0.00	0.26
IP _v	8.11	5.86	6.73	6.37	6.20	6.14	7.14	6.43	6.87	6.19	6.29
XC/SDD											
ΔE	-	-	-	0.00	0.24	0.25	0.00	0.17	0.45	0.00	0.27
IP _v	8.36	6.08	6.96	6.58	6.32	6.28	7.29	6.58	7.03	6.31	6.45

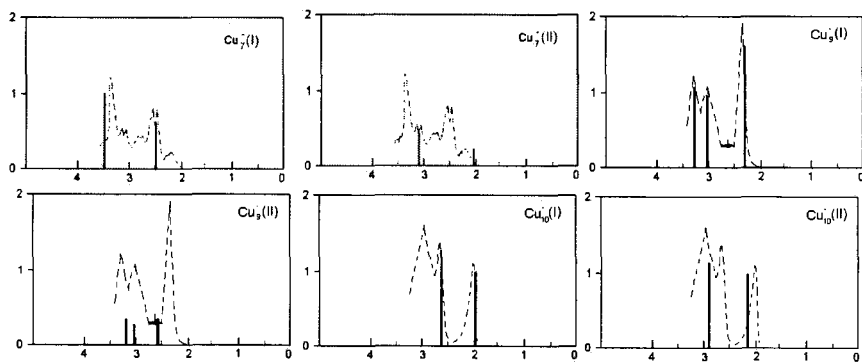


Figure 2. Experimental (dashed line) and XC/LANL2DZ calculated PES of copper clusters.

2.2 Identification of Cu₉ and Cu₁₀ structures

Using XC/LANL2DZ we made a structural assignment of Cu₉⁻ and Cu₁₀⁻ clusters. The assignment of structures of anionic nanomers and decamers has been based on both relative energy calculations and comparison of experimental and calculated PES. The geometrical and energetic characteristics of seven isomers have been calculated for Cu₉⁻ and Cu₁₀⁻ clusters. The initial structures of clusters for geometry optimization were produced in the same manner as for silver clusters [1]. The

calculated and the experimental PES of the most stable isomers are given in Fig. 2 and the predicted equilibrium geometrical structures are presented on Fig. 3. The PES of $\text{Cu}_{10}^-(\text{III})$ is not pictured on Fig. 2 because it considerably differs from the experimental one.

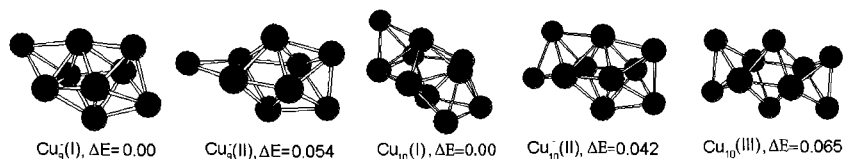


Figure 3. XC/LANL2DZ optimized geometries and relative energies of copper clusters.

According to the calculations, the most stable for Cu_9^- clusters is $\text{Cu}_9^-(\text{I})$ structure. The structure $\text{Cu}_9^-(\text{II})$ with symmetry C_{2v} does not contribute to PES, whereas in the case of silver this structure is the most stable [1]. In common with Ag_{10}^- , for Cu_{10}^- only $\text{Cu}_{10}^-(\text{I})$ structure corresponds to experimental PES.

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ELECTROCHEMICAL DEPOSITION OF METAL SELENIDE CLUSTERS ON SELENIUM SURFACE

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Mechanisms of electrochemical and photoelectrochemical deposition of metal selenide clusters (Me = Pb, Cd, Zn, Bi, In) onto the surface as well as into the selenium films have been studied. These clusters are formed as a result of underpotential and overpotential deposition of the metals onto Se. Photoinduced underpotential deposition of Bi onto Se was used to cover selenium colloidal particles with Bi₂Se₃ clusters. The PbSe and Bi₂Se₃ clusters modify the Se surface and form electronic surface states in the Se bandgap, thus promoting electron exchange processes between the valence band and redox species in solution and the rise of the subbandgap photocurrent.

1 Introduction

The study of metal adatoms deposited onto the surface of semiconductor electrodes is of interest for electrodeposition of epitaxial [1] and textured [2] films and superlattices of metal chalcogenides [3]. In the past decade, an additional interest in processes of underpotential deposition (upd) has been stimulated by the progress in studying physics and chemistry of nanosize objects [4].

In the present work, upd of Pb, Cd, Zn, Bi, In onto Se was used to form the metal selenide clusters on the surface as well as in the bulk of amorphous (*a*-) and polycrystalline (*pol*-)Se.

2 Results and discussion

We have recently reported on possibility of the photoinduced upd of Pb adatoms (Pb_{ad}) onto *pol*-Se electrodes [5]. The process does not occur in dark because of the extended space charge region (SCR) being formed, which hinders the charge transport through the Se|electrolyte interface. The dark current is negligible in the wide potential range from -0.5 to +0.8 V (all potentials in the work were determined with respect to the Ag|AgCl|KCl_(sat) reference electrode). On illumination, electron-hole pairs photogenerated in Se are separated by the field in the SCR. Photoelectrons move towards the electrode surface and reduce metal ions, resulting in the photoinduced upd. Photoinduced upd of Pb, Cd, Zn, Bi and In onto *a*-Se was investigated. A cathode current appears when the Se electrode is illuminated in nitric acid solutions containing Se ions. The potential of the photocurrent onset

depends on the reducing metal. In the case of Pb and Bi it appears at $E \approx 0.4$ V, i.e. at more positive potential than the photocurrent onset in the supporting electrolyte (Fig. 1a).

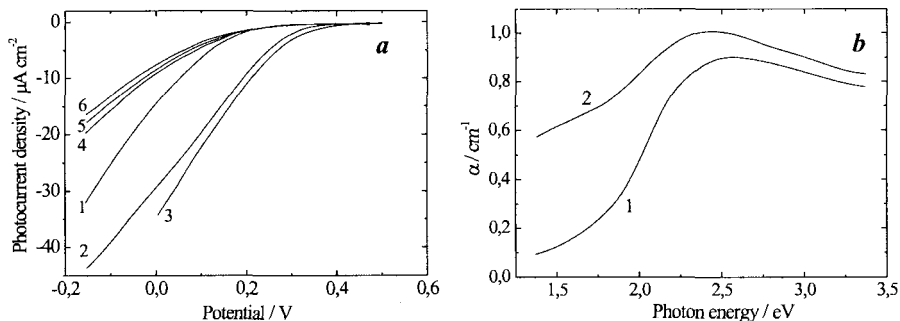


Figure 1. a) Photocurrent vs. potential curves recorded under polychromatic illumination of the Se electrode in 0.1 M HNO_3 (1); 0.05 M Pb(II) + 0.1 M HNO_3 (2); 2 mM Bi(III) + 0.3 M HNO_3 (3); 2 mM In(III) + 0.1 M HNO_3 (4); 0.05 M Cd(II) + 0.1 M HNO_3 (5); 0.05 M Zn(II) + 0.1 M HNO_3 (6). b) Absorption spectra of the Se colloidal solution before (1) and after (2) modification with Bi_2Se_3 clusters.

The photocurrent in Pb(II) and Bi(III) –containing solutions is unsteady and drops sharply by 80-90% after the charge required for the reduction of monolayer of the metal passed through the electrochemical cell. This current drop is a characteristic of the upd processes in general. The interaction of the monolayer with Se results in a metal selenide cluster formation at the Se surface. The clusters were detected by the potential of electrochemical oxidation and rise of the optical absorption of the films in the long-wavelength region (in the case of low bandgap selenide formation), where amorphous Se absorbs negligibly (Fig. 1b).

The range of potentials where the photo upd of Bi(III) onto Se occurs was used for photoelectrochemical deposition of Bi_2Se_3 monolayer onto the surface of Se colloidal particles. The necessary level of electrochemical polarization in this case was achieved by means of Ti(III)/Ti(IV) redox pair introduced into the solution. On illumination, electrons photogenerated in Se particles move towards the surface and reduce the Bi(III) ions. Bismuth adatoms being oxidized with Se form Bi_2Se_3 . It gives a significant rise of absorption in the long-wavelength region, where the colloidal solution of Se absorbs negligibly (Fig. 1b).

Modification of the Se surface both with PbSe and Bi_2Se_3 clusters results in the formation of electron surface states located in the Se bandgap near the valence band edge. Rapid electron exchange between the surface states and the valence band facilitates the codeposition of Se(IV) and Pb(II) in the dark in the potential range ($-0.3 \text{ V} < E < 0.1 \text{ V}$) where the upd of lead appears (Fig. 2a). In this way nanocomposite films consisting of α -Se and nanosized PbSe clusters distributed throughout the whole film were produced (Se/ PbSe -films). X-ray diffraction (XRD) showed that the undoped Se film and Se/ PbSe films with the Pb content < 5 (XRD) at.% were amorphous. At the higher Pb content, XRD peaks of the PbSe

phase appear. These peaks are strongly broadened, which is indicative of a high-disperse state of PbSe. The average size of PbSe crystallites estimated from the XRD peaks half-width is 2-4 nm. Lead cluster formation in the Se films results in a decrease of the photocurrent quantum yield in the wide spectral region up to 550 nm, while a sub-bandgap photoresponse, manifesting itself as a photocurrent tail at $\lambda > 600$ nm, appears for the PbSe clusters-doped Se films in contrast to the undoped ones (Fig. 2b).

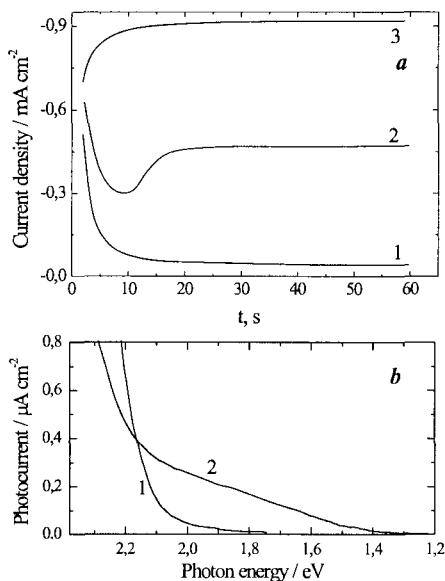


Figure 2. a) Current vs. time during electrodeposition of a-Se onto Au substrate (1) (0.02 M SeO_2 + 0.1 M HNO_3 solution) and Se/PbSe nanocomposites with lead content 0.5 at.% (0.02 M SeO_2 + 0.1 M HNO_3 + $2 \cdot 10^{-5}$ Pb(II) solution, curve 2) and 4.4 at.% of lead (0.02 M SeO_2 + 0.1 M HNO_3 + $2 \cdot 10^{-4}$ Pb(II) solution curve 3). The potential of electrodeposition in all cases was -0.3 V. b) Long-wavelength edge of the photocurrent spectra of the undoped (1) and PbSe-doped (0.5 at. % Pb) a-Se films in 0.1 M HNO_3 solution at the potential of -0.2 V.

Apart from the upd, the process of overpotential deposition (opd) of metals might be used for metal selenide clusters formation. In contrast to the upd, bulk particles of metal (Me_{bulk}) are formed in the latter case. The formation of metal selenide clusters occurs because of oxidation of the metal particles with Se can proceed at the places where Me_{bulk} particles are in contact with the surface Se atoms, i.e. on $\text{Se}|\text{Me}_{\text{bulk}}$ interface (Fig. 3a). The electrodeposition of Pb onto *pol*-Se electrode appears at $E < -0.4$ V (Fig. 3b) and results in Pb_{bulk} particles formation on the surface. The reversible potential of Pb electrode in the same solution is -0.37 V, i.e. Pb_{bulk} is cathodically deposited on the Se electrode in the opd regime. The anodic peak B corresponds to the stripping of bulk Pb. The anodic peak A_1 is associated with Pb_{ad} stripping. Peaks A_2 and A_3 are due to the PbSe cluster oxidation ($\text{PbSe} - 2e = \text{Pb(II)} + \text{Se}$). It should be noted that the charges for A_2 and A_3 peaks are $380 \pm 40 \mu\text{C}/\text{cm}^2$ which is comparable to the charge of Pb_{ad} monolayer oxidation (A_1 peak).

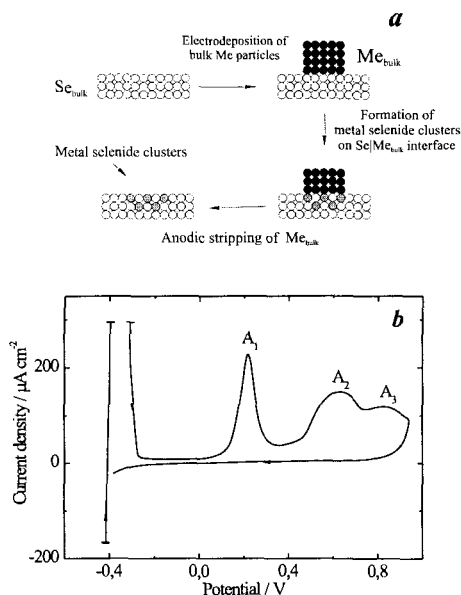


Figure 3. a) Scheme demonstrating metal selenide clusters formation in the Se|Me_{bulk} interface due to the chemical oxidation of metal with Se. b) Voltammogram of the Se electrode in 0.05 M Pb(II) + 0.1 M HNO₃ solution. Potential scan rate: 20 mV s⁻¹.

Another way of formation of metal selenide clusters can be the chemical interaction of cathodically generated H₂Se with metal ions from the solution ($\text{H}_2\text{Se} + \text{Me(II)} = \text{MeSe} + \text{H}^+$). Hydrogen selenide may be formed on the Se-electrode surface via the reduction of Se with photoelectrons ($\text{Se} + 2\text{H}^+ + 2e_{\text{ph}} = \text{H}_2\text{Se}$). The clusters of PbSe, CdSe, ZnSe, In₂Se₃, Bi₂Se₃ were successfully synthesized in this way.

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INVESTIGATION OF MONOLAYERS BY POTENTIODYNAMIC ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Te and Cu monolayers on gold, as well as Ag and Bi monolayers on platinum were obtained by cathodic underpotential deposition and investigated *in situ* by the potentiodynamic electrochemical impedance spectroscopy (PDEIS). PDEIS gives the graphical representation of the real and imaginary interfacial impedance dependencies on ac frequency and electrode potential in real-time in the potential scan. The built-in analyzer of the virtual spectrometer decomposes the total electrochemical response into the responses of the constituents of the equivalent electric circuits (EEC). Dependencies of EEC parameters on potential, especially the variation of capacitance and pseudocapacitance of the double layer, appeared to be very sensitive indicators of the interfacial dynamics.

The electrochemical monolayer deposition in cathodic reactions above the Nernst potential, the underpotential deposition (UPD), is one of the most promising instruments for assembling of nanostructures from atoms and atomic monolayers [1]. Though the UPD phenomenon has been known for decades [2], its technological application is still hindered, because of insufficient knowledge of the dynamics and mechanisms of reactions in the monolayers.

PDEIS [3] is expected to promote better understanding of reactions in the monolayers and their real-time control. Our expectations are grounded on the following qualities of this technique: (i) the capacity for the monolayer *in situ* with high temporal and electrode potential resolution; (ii) the sensitivity to products of adatoms interaction with surrounding medium, e.g. anion adsorption; (iii) the electrochemical nature of the technique that makes its application convenient in the UPD investigation and control.

PDEIS is a new technique based on fast measurements of the interfacial impedance with the virtual instruments [3] that benefits from the efficient synchronization of direct hardware control and data processing in the real-time data acquisition and control [4]. The built-in EEC fitting engine of the virtual spectrometer divided the total electrochemical response into its constituents those result from different processes. Thus, just in the electrochemical experiment, we come from the mountains of raw data to the characteristics of the constituent processes – the potential dependencies of the electric double layer capacitance, charge transfer resistance, impedance of diffusion, adsorption, etc. The power of this approach results from different frequency and potential dependencies of the constituent responses. Because of the uniqueness of each UPD system and complex electrochemical response dependence on the frequency and electrode potential, the transition from the PDEIS spectrum (Nyquist or Bode plot expanded to the 3D plot

by the variable potential) to the properties of monolayer chemistry becomes straightforward. We illustrate this on various UPD systems investigated with PDEIS.

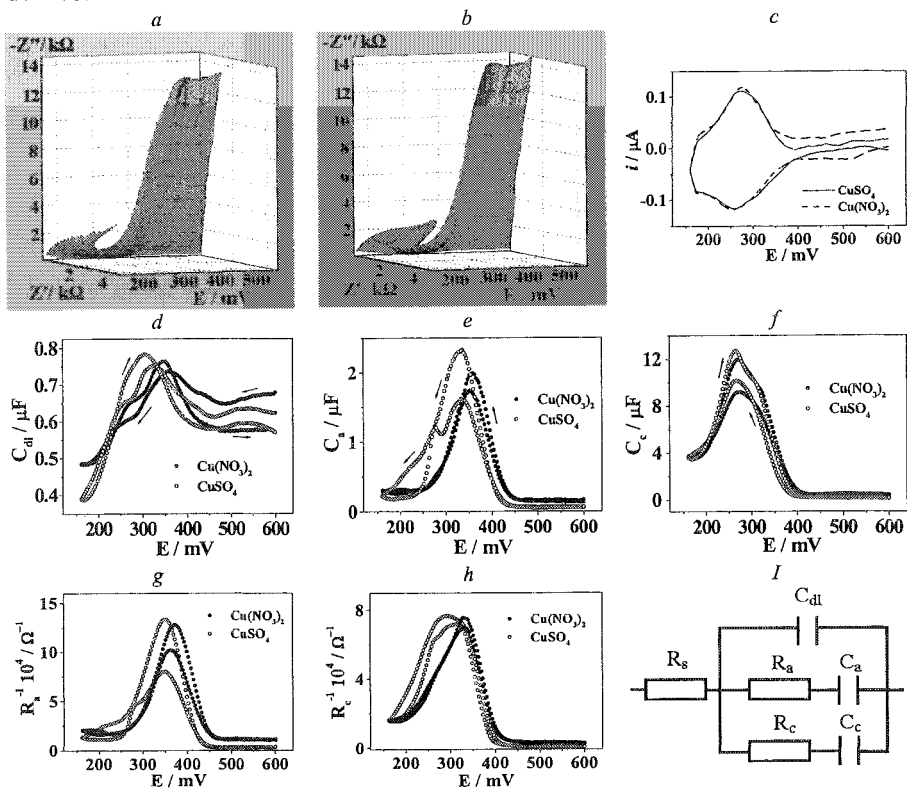


Figure 1. Cu UPD on Au. (a, b) PDEIS spectra, (a) cathodic, (b) anodic branch of the cyclic potential scan in 0.1M H_2SO_4 +10mM CuSO_4 ; (c) cyclic voltammograms of Au in 0.1M H_2SO_4 +10mM CuSO_4 and 0.1M HNO_3 +10mM $\text{Cu}(\text{NO}_3)_2$; (d-h) the dependencies of EEC parameters on potential; (i) the EEC obtained from the PDEIS spectra. $dE/dt = 2 \text{ mV/s}$.

Figs. 1-4 show the original PDEIS spectra and some derivative dependencies that characterize Cu (Fig.1) and Te (Fig.2) monolayers electrochemical formation and their destruction on the annealed polycrystalline gold and also formation of Ag (Fig.3) and Bi (Fig.4) monolayers on the annealed surface of polycrystalline platinum. The abbreviations in the PDEIS spectra and EECs have the following meaning: Z' – real impedance, Z'' – imaginary impedance, E – electrode potential vs Ag/AgCl reference electrode, C_{dl} – double layer capacitance, R_s – solution resistance, R_c and C_c – pseudoresistance and pseudocapacitance of the monolayer electrochemical adsorption/desorption, R_a and C_a – pseudoresistance and pseudocapacitance of the conjugated adsorption/desorption of the anions, R_{ct} –

charge transfer resistance, W – Warburg element (impedance of diffusion), CPE – constant phase element. The latter element represents the double layer pseudocapacitance Q_{dl} defined by the following relation between CPE impedance Z_{cpe} , circular frequency ω , imaginary unit j and fractional exponent n (n was close to unity):

$$Z_{cpe}=Q_{dl}^{-1}(j\omega)^{-n}$$

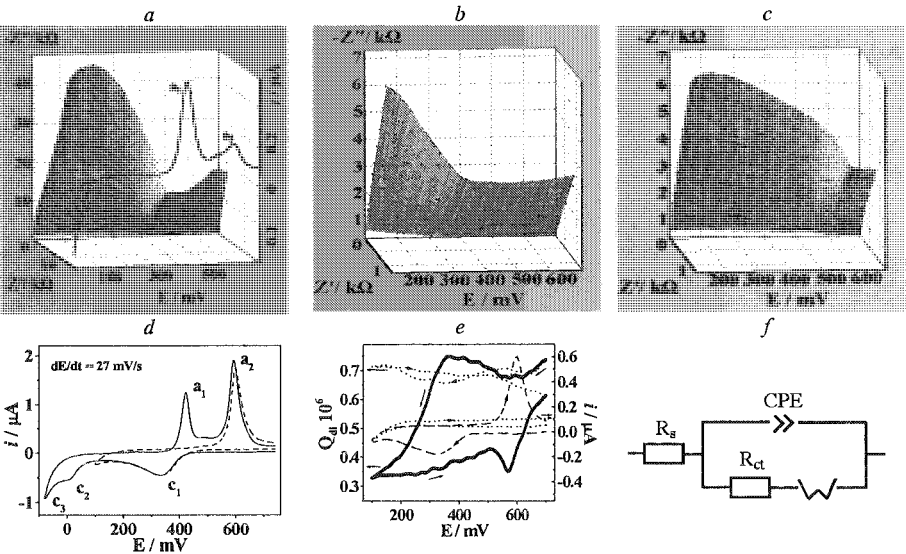


Figure 2. Tellurium UPD on Au in 0.1M H_2SO_4 +2mM TeO_2 . (a) PDEIS spectrum and the voltammogram for combined Te nanoparticles (a_1) and monolayer (a_2) oxidation in the anodic scan; (b,c) PDEIS spectra of Te monolayer, (b) cathodic, (c) anodic scan; (d) cyclic voltammograms with different reversal potentials; (e) Q_{dl} dependence on potential (solid circles) and cyclic voltammogram (dashed). Dotted lines show the reference dependencies in absence of Bi. (f) EEC. $dE/dt = 7.6$ mV/s except for (d).

The variation of the EEC parameters with the potential shows some correlation with the cyclic voltammograms and additionally gives much information that could not be obtained in dc probing of the interface, as well as by the potentiostatic impedance spectroscopy: fine effects of the anions, the potentiodynamic transformations in the double layer between the potentials of monolayer formation and destruction, etc. In the conference report we discuss the perspectives for the monolayer chemistry that arise from these new experimental facilities.

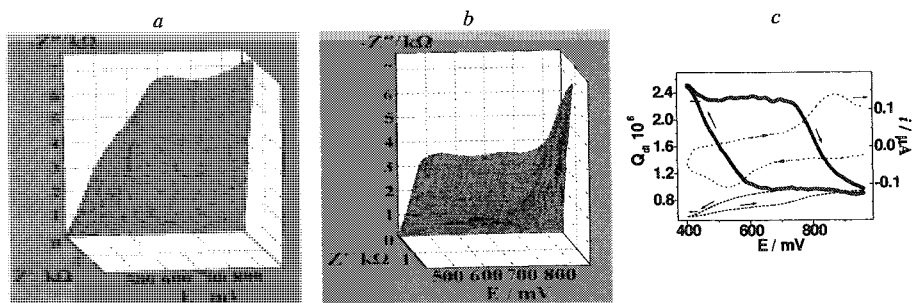


Figure 3. Ag UPD on Pt in 0.1M HNO_3 +1mM AgNO_3 . (a, b) PDEIS spectra, (a) cathodic, (b) anodic scan; (c) Q_{dl} dependence on potential (solid circles) and the cyclic voltammogram (dotted). The dashed line shows the reference Q_{dl} in absence of Ag. $dE/dt=2.6$ mV/s.

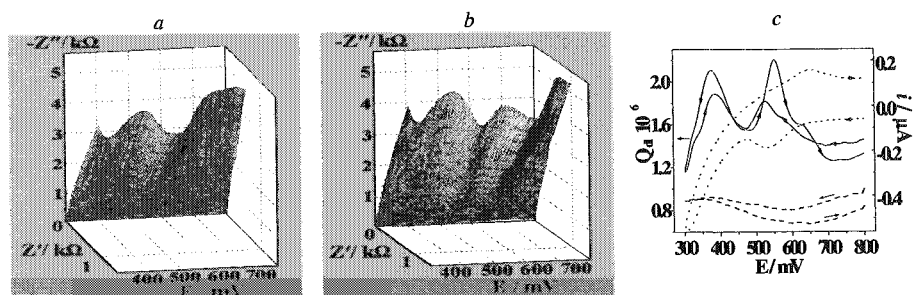


Figure 4. Bi UPD on Pt in 0.3M HNO_3 +5mM $\text{Bi}(\text{NO}_3)_3$. (a, b) PDEIS spectra, (a) cathodic, (b) anodic scan; (c) Q_{dl} dependence on potential (solid) with the corresponding cyclic voltammogram (dotted). The dashed line shows the reference Q_{dl} in absence of bismuth. The EEC is the same as in Fig. 2. $dE/dt=2.6$ mV/s.

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SELF-FORMING OF SILICON SURFACE NANORELIEF NEAR EDGES OF CHEMICAL MASKS DURING ANISOTROPIC ETCHING

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The influence of concentration, temperature of KOH solutions and isopropanol addition on type of Si-nanoplanes self-formed in the course of etching near convex right angles of oxide masks, the sides of which are oriented in various crystallographic directions on Si (100) surface is investigated.

1 Introduction

Anisotropic etching is one of the key processes in fabrication of promising nanodevices based on monocrystalline silicon. It makes possible to obtain micro- and nano-details of well-defined forms by the use of chemical masks, having various crystallographic directions. For elaboration of high-efficiency nanotechnology stages it is necessary to investigate features of the crystal dissolution near edges of the mask. In spite of certain advances in silicon micromachining, a mechanism of surface relief formation under anisotropic etching remains unknown in detail.

There is also a lack of reliable empirical data concerned with the peculiarities of self-forming such individual elements of the relief as facets, edges and cones of micro- and nano-dimensions. Up to now there are discrepancies between experimental results on nanorelief formation near convex right angles of the chemical masks on Si(100)-surface in KOH-water solutions which are the most usable anisotropic etchant in micromachining technology. For example in different works appearance of dissimilar sets of micro- and nano-planes with various orientations (hkl) were observed under similar etching conditions [1-4]. In addition to our previous results [3], in the present paper more definite information about this self-forming process over the more wide range of the experimental conditions was obtained.

2 Experimental

Etching was carried out at 60 and 80°C ($\pm 0.02^\circ\text{C}$) in KOH aqueous solutions (8-14 mol/l), and also in KOH solutions of the same concentrations added with isopropanol (IPA) up to saturation. Samples of single-crystal silicon of p-type

12 Ohm-cm were used in the experiments. Sample surfaces (001) were covered with oxide masks of a “square” type (Fig. 1). After etching under the definite condition the surface nanorelief near angles of the mask squares was investigated with the use of scanning electron microscope (SEM) and optical microscope which were equipped with precise goniometers. In all experiments h/k -ratio of the emerging nanoplanes was determined. Examples of such nanoplanes one can see in Fig. 2. The plains 1 and 4 emerging near the linear sides of the masks are known as (111) and (100) for Fig. 2a and Fig. 2b, respectively [1-4]. In our new experiments it was again proved to be true.

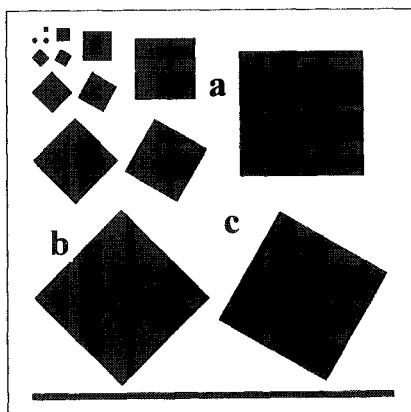


Figure 1. An oxide mask of “square” type: a), b) and c) – rows of oxide squares of different area with side orientation like $[110]$, $[100]$ and $[100] + 30^\circ$, respectively.

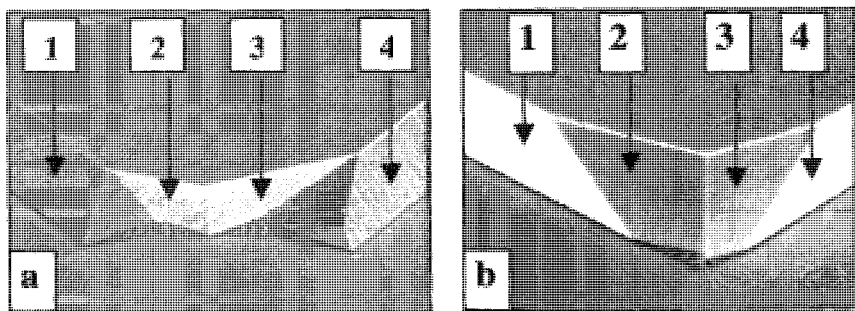


Figure 2. Typical SEM images ($\times 10000$) of the nanoplanes arising as a result of underetching of right angles of the square mask, the sides of which are aligned with crystallographic $[110]$ (a) and $[100]$ (b) directions.

Crystallographic orientation of the two other planes "2" and "3" was changed according to variation of etching conditions. The attention in the work has been given to these latter nanoplanes (Fig. 2). The main experimental result is a dependence of k/h-ratio on experimental condition namely for these nanoplanes associated with [110]- and [100]- squares of the mask. The results are listed in the Table 1.

Table 1. Dependence of h/k-ratio for "2" and "3" self-formed nanoplanes (fig.2) associated with [100]- and [110]-mask squares on experimental conditions.

Solution	Concentration of KOH, mol/l	Temperature of etching	h/k: [100]	h/k: [110]
KOH	8	60°C	0.34	0.24
KOH	10	60°C	0.31	0.24
KOH	12	60°C	0.32	0.25
KOH	14	60°C	0.35	0.22
KOH/IPA	8	60°C	0.44	0.38
KOH/IPA	10	60°C	0.34	0.31
KOH/IPA	12	60°C	0.31	0.26
KOH/IPA	14	60°C	0.35	0.23
KOH	8	80°C	0.35	0.22
KOH	10	80°C	0.35	0.29
KOH	12	80°C	0.36	0.29
KOH	14	80°C	0.35	0.23
KOH/IPA	8	80°C	0.28	0.40
KOH/IPA	10	80°C	0.33	0.33
KOH/IPA	12	80°C	0.36	0.29
KOH/IPA	14	80°C	0.35	0.24

It is apparent that temperature of aqueous KOH solutions and also KOH+IPA-solutions does not influence essentially the type (orientation of an "upper" edge) of the nanoplanes investigated. Concentration of KOH in the aqueous solutions influences the nanoplane type also unessentially. In particular, it is established that near the right angles of [100]- mask squares h/k - ratio is within the range of 0.31-0.36. For the mask squares of [110]-type this range is from 0.22 to 0.29.

The effect of IPA addition to the KOH solution on the self-formation process was as follows. At low concentrations of KOH the addition of IPA makes distinct influence on type of the self-formed nanoplanes. At high concentrations of KOH (12-14 (mol/l)) the influence of the IPA is unessential (Table 1).

In KOH+IPA solutions the variation in KOH concentration had a pronounced effect on the type of the self-forming nanoplanes. It is established that the change in

KOH concentration in the experimental range brings to h/k-variation from 0.28 to 0.44 for the nanoplanes self-formed near the angles of [100]-mask squares and from 0.23 to 0.40 for the nanoplanes formed near right angles of the [110]-squares.

3 Conclusions

a) A weak dependence of the nanoplane type, characteristic of Si-etching in the solutions with high KOH concentration, on IPA content is connected with decreasing of IPA dissolubility under the gain in concentration of KOH.

b) Essential distinction between types of nanoplanes self-formed in KOH solutions of low concentrations and in KOH (the same concentrations) +IPA - solutions is associated with steric peculiarities for adsorption of alcohol molecules which are the barriers to attack of the silicon surface by particles of etchant. The adsorption efficiency essentially depends on orientation of the crystal surface. In all experiments the nanoplanes with the maximum etching rate characteristic of given IPA concentration stand out in nanorelief.

c) The measured h/k ratios are not the exact ratio of small integers (e.g. 1/2, 1/3, 2/3) as it was reported previously [1,2,4]. It is possible that this divergence is due to an influence of fine structural features in a volume of the starting Si-crystals upon nanoplane orientation.

The obtained data may be used in developing of silicon nanotechnology, in particular, in designing chemical masks with compensation of truncating of convex angles during anisotropic etching. The obtained results should be taken into account in the single-crystal dissolution theory.

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FORMATION OF SILVER NANOPARTICLES FROM A (2,3-DYHYDROXY-4,6-DI-TERT-BUTYLPHENYLTHIO-)ACETIC ACID SILVER COMPLEX

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The silver reduction from the Ag(L)_2 complex (where $\text{L}=2,3\text{-dyhydroxy-4,6-di-tert-butylphenylthio-})$ acetic acid was studied in various electron donor media. Formation of silver nanoparticles was monitored by atomic force microscopy (AFM) and optical absorption UV-visible spectroscopy.

1 Introduction

Silver reduction from its complex precursors is of interest to produce silver nanoparticles [1,2]. Metal colloids can be stabilized by functional groups in polyelectrolytes and surfactants [1]. The stabilization is a useful method for the directional drug delivery and the prolongation effect.

Among a number of pyrocatechol derivatives being potential reducing agents we have found the compound which does not reduce silver. The complexation prevents the redox reaction. Interaction of silver ions with (2,3-dihydroxy-4,6-di-tert-butylphenylthio)-acetic acid (L) results in formation of the Ag(L)_2 complex.

2 Methods

The adsorption of Ag(L)_2 complex was carried out from its solutions (in benzene, ethanol, dimethylformamide (DMF)) of different composition on the solid silicon substrates using the layer-by-layer self-assembling method. Behavior of Ag(L)_2 in ethanol and DMF was studied. The physical properties of these solvents, in particular, donor numbers and dielectric constants are rather different [3].

Silicon substrate was modified by alternative adsorption of 1 mg/ml polyelectrolyte solutions. Positively charged poly-(diallyldimethylammonium chloride) (PDDA, $M_w=200000\text{-}350000$, Aldrich) and negatively charged poly-(sodium 4-styrenesulfonate) (PSS, $M_w=70\ 000$, Aldrich) served as polyelectrolytes. The treated surfaces were rinsed with pure water 3-5 times between each layer

deposition step. The outermost layer became negatively or positively charged after the treatment with PSS and PDDA, respectively.

AFM images of surface morphology and particle size were obtained with FemtoScan 001 (Advanced Technologies Center, Moscow) operated in the constant force mode (1-10 nN) using nanoprobe cantilevers (spring constant 0.32 N/m) with oxide-sharpened Si_3N_4 integral tips.

3 Results and discussion

Treating of the positive charged silicon substrate with benzene solution of the $\text{Ag}(\text{L})_2$ complex (0.5 mg/ml) did not result in a surface morphology change (Fig. 1). The aggregated structures of few tens of nanometer height can be referred to contamination. The 5 times increasing of the complex content in benzene solution produced no essential changes. This experimental fact can be described as either absence of the charge of molecules that prevents effective absorption onto the charged surface of substrate or small sizes of the complex particles.

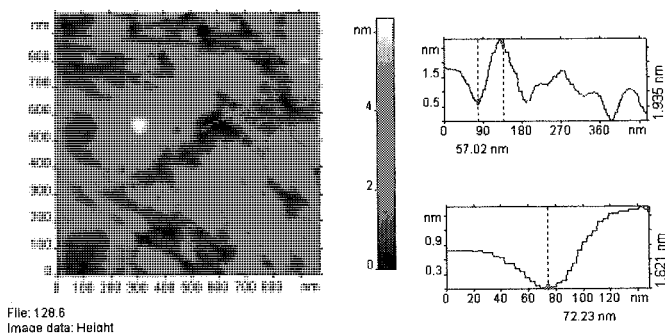


Figure 1. AFM image of the silicon substrate modified with polyelectrolytes and treated with benzene solution of the $\text{Ag}(\text{L})_2$ complex (2.5 mg/ml).

A dissolution of the complex in ethanol (Fig. 2a) and DMF (Fig. 2b) (1 mg/ml) results in its destruction accompanied by oxidation of pyrocatechol and reduction of silver with formation of colloid. Silver particles were adsorbed on the positively charged surface of the substrate. Particle size can be varied between ~20 nm in ethanol and ~50 nm in DMF.

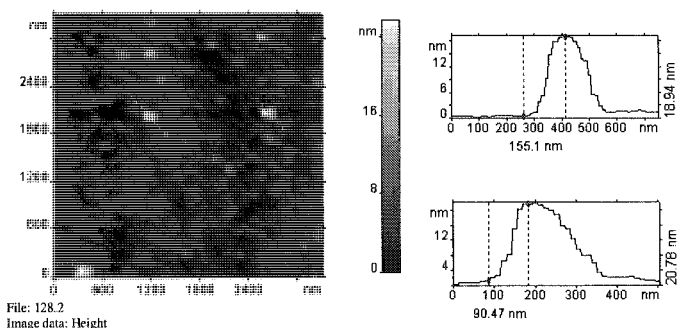


Figure 2. AFM images of silver particles reduced from the $\text{Ag}(\text{L})_2$ complex in ethanol.

The images recorded were compared the results on reduction of silver ions by ascorbic acid (Fig. 3). The similarity of shape and size of silver nanoparticles produced from the above complex and with the external reducing agent is observed.

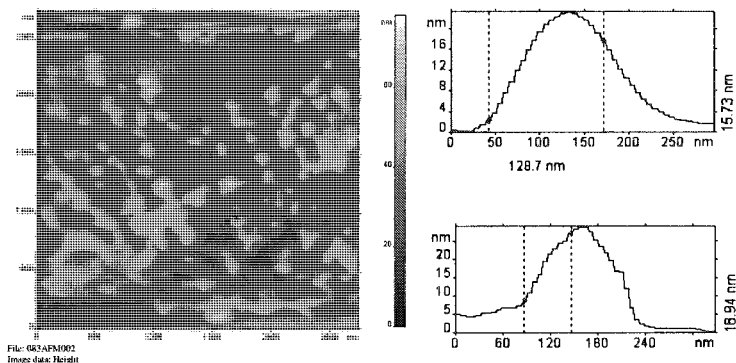


Figure 3. AFM image of silver colloids produced during the reduction of silver nitrate by ascorbic acid.

The degradation of the silver complex transforming to the silver colloid proceeds in different ways depending on the solvent used. This is illustrated with the optical absorption spectra (Fig. 4). In the ethanol medium the formation of silver colloid is slow and was not completed during the time interval studied. The plasmon band position blue shifts during the reaction for this system due to the absorption of unreacted silver ions on the surface of colloid particles. Coarse silver particles are formed during two days. In DMF medium silver colloid appears immediately after dissolution of $\text{Ag}(\text{L})_2$. The process is intensified because DMF is a strong reducing agent for silver ions [4]. Yellow sol produced is stable during more than 10 days. The spectrum peaks at $\lambda \sim 420$ nm, that is a characteristic of silver colloids. The temporal evolution of the spectrum (brodening, red shift, lowering of intensity) reflects the processes of particle growth and adsorption of organic compounds on the surface of particles.

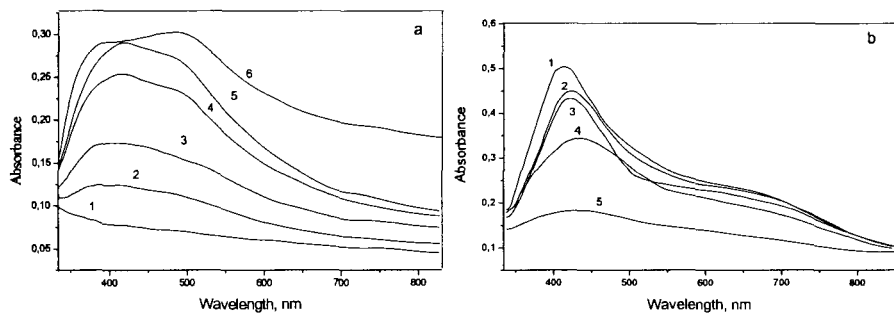


Figure 4. Time evolution of the UV-visible spectra of silver nanoparticles prepared by $\text{Ag}(\text{L})_2$ decomposition in ethanol (1 – freshly prepared solution, 2 – 5 min, 3 – 25 min, 4 – 45 min, 5 – 55 min, 6 – 105 min) (a); in DMF (1 – freshly prepared solution, 2 – 40 min, 3 – 120 min, 4 – 4 days, 5 – 10 days) (b).

It should be noticed that at final steps of the process these both systems became similar owing formation of a silver precipitate of the aggregated particles (Fig. 2b). The absorption spectrum has the maximum specific to the ligand oxidation product.

In conclusion, (2,3-dihydroxy-4,6-di-tert-butylphenylthio)-acetic acid forms a stable crystalline complex with silver (I) ions. The complex is capable to produce stable silver nanoparticles as the result of reduction.

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FORMATION OF THIN SOL-GEL NANOCOMPOSITE Ag-GeO₂ FILMS

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The work considers processes in Ag⁺-GeO₂ film systems under heating them in air which result in nanocomposite "Ag-GeO₂" film formation. The silver nanoparticles are produced due to the thermostimulated interaction of silver ions with the oxide matrix yielding silver germanate, which decomposes at above 700°C to form silver nanoparticles and germanium dioxide.

1 Introduction

Composite film coatings comprising nanodisperse silver are under intensive investigation nowadays being of interest as promising electroconductive metal-polymer systems, nonlinear optical materials, selective and active catalysts.

One way to fabricate "silver-oxide" films is the sol-gel method, which gives silver nanoparticles in oxide matrices formed by thermal reduction of silver-ion-containing films in a hydrogen flow [1-3]. There is information on production of silver nanoparticles in SiO₂ films for the atomic ratios Ag:Si ≥ 0.12 by heating them in air at 500-600°C [4,5]. Our preliminary experiments for "Ag⁺-SiO₂" and "Ag⁺-GeO₂" systems have shown that formation of silver nanoparticles in these cases could proceed via thermostimulated silver ion interaction with the oxide matrix yielding a new phase, silver silicate or germanate, which was thermally decomposed resulting in nanosized silver particles. The paper presents results of the investigation of the thermostimulated silver nanoparticle formation in the sol-gel GeO₂ films in air.

2 Method

To produce "Ag⁺-GeO₂" films, stable GeO₂ sols doped with silver ions (Ag:Ge=0.12 at.%) were used. GeO₂ sols were prepared by water hydrolysis of GeCl₄ (chemically pure). The precipitate formed was washed and peptized by adding concentrated nitric acid down to pH=6 or aqueous ammonia up to pH=9 under ultrasound treatment. Four-layer films were spin-coated layer-by-layer onto quartz substrates heated in air at 150°C for 10 min after coating of each layer, followed by heating in air in a cumulative mode (1 h at each temperature) at 350°C, 500°C, 600°C and 800°C.

Optical absorption spectra of the films in the wavelength range of 200-900 nm were registered using a SPECORD M40-UV-VIS spectrophotometer. Morphology and dispersion of the particles were examined by the transmission electron microscopy (TEM) with an EM-125K instrument. X-ray diffraction (XRD) analysis of the powders separated from the initial "Ag⁺-GeO₂" sols was carried out with a DRON-3.0 diffractometer using CoK_α radiation. The processes during heating of the powders in air were examined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) with a F. Paulik, G. Paulik, L. Erdey derivatograph up to 800°C at the heating rate of 5 K/min.

3 Results and discussion

Optical absorption spectra for "Ag⁺-GeO₂" films are presented in Fig. 1. Their evolution with the heating temperature is the same for the films produced from different sols. The initial layers heated at 150°C are colorless and do not absorb in the wavelength range investigated. They become brown on heating at 350°C while a broad absorption band peaking at 440-450 nm appears. On further heating at 500°C and 600°C the films gradually become lemon-yellow while the absorption band maximum is blue-shifted by 15-30 nm, and it is at 410-415 nm after heating of the films at 800°C.

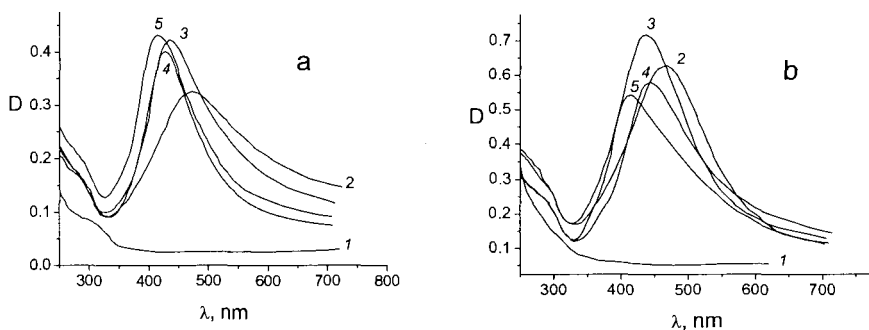


Figure 1. Optical spectra of "Ag⁺-GeO₂" films formed from ammonia (a) and nitric acid (b) composite sols and heated at 1-150°C, 2-350°C, 3-500°C, 4-600°C, 5-800°C.

The powders separated from ammonia "Ag⁺-GeO₂" sols are amorphous according to DTA data. DTA and TGA curves show endothermic effects with the minima at 100°C and 230°C accompanied by weight losses of 10% and 5%, respectively, as well as exothermic effects with the maxima at 350-370°C, 470°C and 770°C accompanied by slight weight losses of the samples. The endoeffects are due to water and ammonia removal, respectively. The exoeffects (also according to XRD) are due to crystallization of hexagonal GeO₂ and formation of silver

germanate ($\text{Ag}_2\text{Ge}_4\text{O}_9$) phases, respectively, and decomposition of the germanate forming tetragonal GeO_2 and silver. Note that the brown color appears both in the powders and in the films even at 350°C which may be indicative of the silver germanate starting to form at that temperature.

Hexagonal GeO_2 phase was detected also in the unheated powders prepared from the nitric acid " Ag^+-GeO_2 " sol. The DTA and TGA curves for these samples show endoeffects with minima at 90°C and 220°C , accompanied by weight losses of 9% and 7%, respectively, as well as exoeffects peaking at 260°C , 440°C and 730°C with slight weight losses of the samples. The endoeffects are due to elimination of water and decomposition of nitric acid. The exoeffects (considering the XRD data) can be attributed to crystallization of hexagonal GeO_2 , formation of silver germanate and its decomposing. Note that in the " Ag^+-GeO_2 " sample produced from GeO_2 sol peptized with nitric acid the thermostimulated processes take place at lower temperatures as compared to the sample produced from NH_3 -peptized " Ag^+-GeO_2 " sol.

Based on XRD studies we can say that the optical absorption of the films heated at 350 – 500°C is due to silver germanate, while the features in the films heated at 800°C belongs to silver nanoparticles (Fig. 1).

TEM for the films heated at 800°C shows an appearance of uniformly distributed spheroidal particles observed on the background of the GeO_2 particles replica. Their size ranges from 10 to 45 nm, no matter which precursor sol was used. Fig. 2 shows the size distribution and TEM image of the particles in the film formed from the ammonia " Ag^+-GeO_2 " sol and heated at 800°C . Note that particle sizes in the micrograph are about the same as those calculated from the optical spectra of " $\text{Ag}-\text{GeO}_2$ " films heated at 800°C . TEM results for the films at different stages of the heat treatment will be given in more detail in future publications.

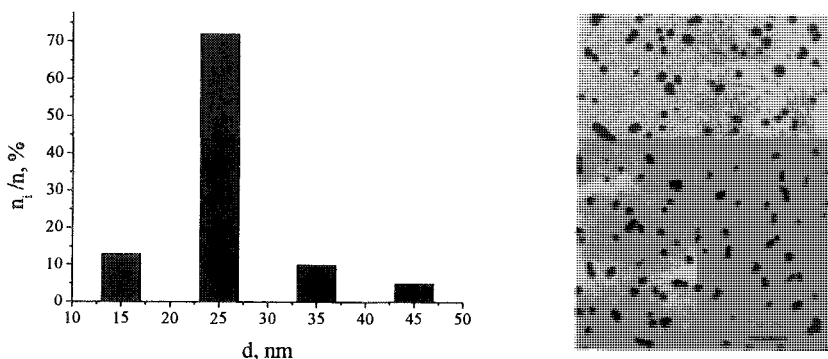


Figure 2. TEM image and particle size distribution for " $\text{Ag}-\text{GeO}_2$ " film formed from ammonia composite sol and heated at 800°C .

4 Conclusion

Our study has demonstrated that formation of silver nanoparticles in "Ag⁺-GeO₂" system proceeds through the decomposition of silver germanate formed after the earlier steps of film heating. That mechanism provides a considerable stability of Ag nanoparticles to oxidation on heating up to 900°C, suggesting that the silver particles are encapsulated by the matrix.

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SOL-GEL SYNTHESIS OF Fe-CONTAINING SILICA GLASSES

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Fe-doped glasses and composites were prepared by hybrid sol-gel process, modified in the part of doping technique. The UV-VIS spectra and XRD-investigation show both the presence of oxide and fluoride complexes in the glass matrices.

1 Introduction

Fe-containing silica glasses and nanocomposites can be used as ferromagnetic materials and colored filters. Utilization of the sol-gel process for synthesis of silica glass is preferable because of its low sintering temperature and high efficiency [1]. Incorporation of fluorine into xerogel simultaneously with Fe-ions reduces bubble formation upon consolidation by sintering and results in the formation of Fe-containing clusters in the network of silica gel-glass.

2 Methods

Fe-doped glasses and composites were prepared by a hybrid sol-gel process [2], modified in the part of doping technique. The flowchart of the hybrid sol-gel process incorporates the following stages: tetraethoxysilane (TEOS) hydrolysis in the system $\text{Si}(\text{OC}_2\text{H}_5)_4$ - $\text{C}_2\text{H}_5\text{OH}$ - H_2O - HCl with mole ratio 1:2:16:0.01 by vigorous mixing in fluoroplastic reactor in air; addition the fumed silica with a specific surface $200 \text{ cm}^2/\text{g}$ into the sol as filler, ultrasonic dispergation and centrifugal separation from agglomerates and dust particles. Then, the sol was neutralized up to $\text{pH}=6.5$ with the help of ammonia solution and cast into fluoroplastic moulds to prepare the solid gels shaped as disks. The wet gels were formed during 20-30 min in sealed containers; then the containers were opened and the gels were washed by bidistilled water.

The resulting gels were dried slowly at $30\text{-}60^\circ\text{C}$ in the period of 7-14 days in air and presintered at 600°C in 2 h. After heat-treatment the xerogels were impregnated by water or organic solutions of $\text{Fe}(\text{NO}_3)_3$ and FeCl_3 .

Using of Fe-containing aqueous solutions for xerogels impregnation results in the preparation of hydroxylated silica gel-glass doped ferrum(III). The presintered

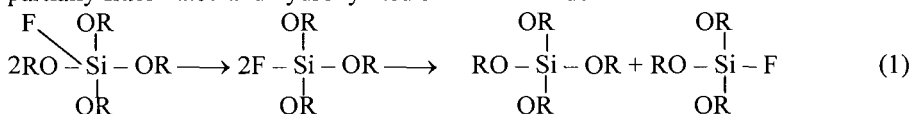
xerogels impregnated by the organic solutions (mixture: acetone, HF) and then by the acetone solution of FeCl₃ lead to the formation of opalescent composites. The following thermo-treatment of Fe-containing porous materials at 1200°C in air lead to formation of silica glass.

3 Results and discussion

Optical absorption spectra were measured using the glass and composite samples of 2-4 mm thickness in the IR, visible- and UV-regions. The pore-size distribution in the gel structure measured by BET-method has a complex character: the network contains micro- (3.0 nm), meso- and macro-pores (5-25 nm). The pore size can be increased by chemical attack of silica network by fluorine ions in solution and also in vapor phase until heating and dissociation of F-containing compounds (HF, NH₄F).

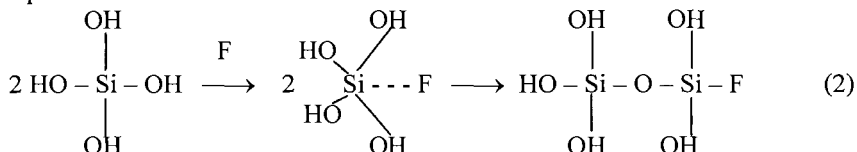
Hydroxyl content in dense glasses and composites was evaluated from IR-absorption spectra using the relationship [3]: $[\text{OH}]\text{ppm} = (1000/t) \log(T_a/T_b)$, where t is the sample thickness (mm), T_a is the transmission at 2.2 μm , T_b is the transmission at 2.72 μm .

The reaction (1) shows that fluorine severely catalyses hydrolysis reaction [3]. In the hydrolysis reaction, because of the smaller ionic radius of the fluorine, which approaches a molecule of TEOS in the solution forming a highly unstable pentacovalent activated intermediate. This complex rapidly decomposes, forming a partially fluorinated and hydroxylated silicon alkoxide.

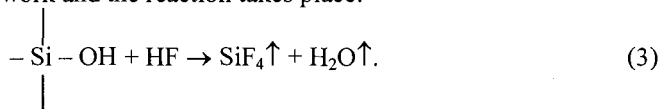


This process can continue until nearly all of the ethoxide bonds are replaced by OH. More that likely, however, the polymerization reaction begins before all TEOS is fully hydrated.

The polymerization reaction forms a hexacovalent intermediate, it rapidly decomposes as follows:



The process of gas-phase fluorine doping reduces hydroxyl level in the xerogels by the attack of gel network and the reaction takes place:



The impregnation of fluorine-containing gels by the acetone solution of FeCl_3 and subsequent thermal treatment at 1200°C in air results in the formation of fluorinated Fe-containing compounds in the form of nanosize amorphous clusters, dispersed in the matrix of silica-like opalescence material.

The IR-spectrum of composite samples demonstrates the hydroxyl groups on the level of 100-150 ppm (Fig. 1). The UV-vis transmission spectra of Fe-containing glasses and composites are shown in Fig. 2.

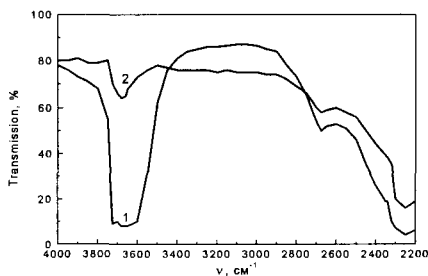


Figure 1. IR-spectra of composite and glass samples: 1 – silica gel-glass; 2 – FeOF_x containing composite.

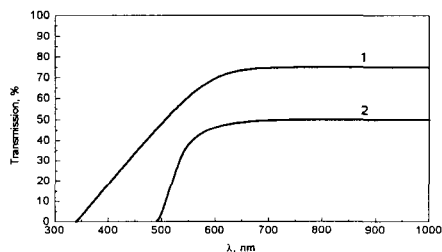
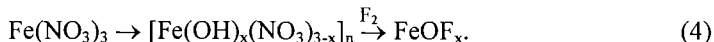


Figure 2. The transmission spectra of Fe-containing glasses(1) and composites(2).

The scheme of Fe-ions transition in impregnated xerogels is probably following:



The incorporation of Fe(III) into the silica matrix was verified by UV-vis spectra. A Fe(III) ion incorporated into the silica network demonstrates the broad band below 350 nm with diffuse edge and Fe-containing composites demonstrates UV-absorption edge shifts to longer wavelength. The absorption band at ~ 500 nm has been attributed to the presence of FeOF_x -complexes in the structure of silica composite.

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STRUCTURE AND OPTICAL PROPERTIES OF $\text{CdSe}_x\text{Te}_{1-x}$ IN GLASS MATRIX

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$\text{CdSe}_x\text{Te}_{1-x}$ nanoparticles were fabricated within the silicate glass matrix and studied with TEM and optical spectroscopy both for as-prepared and heat-treated samples at temperatures lower than the glass softening. Appearance of spectral features in CdTe- and other Te-containing nanoparticles is explained as the phase transformation between wurtzite and sphalerite lattices in the CdSe-CdTe system.

1 Introduction

Silicate glasses activated by cadmium chalcogenides have selective absorption in the visible range. Corresponding cadmium compounds are stable under ambient conditions and in the temperature range of glass preparation, they are inert with respect to glass matrix. Semiconductor nanoparticles formed from the dopants responsible for the optical features are also of great interest for analysis of quantum-size effects [1,2]. However, CdTe as well as the solid solutions with it ($\text{CdSe}_x\text{Te}_{1-x}$) are the less studied among these compounds. Meanwhile, CdTe is rather different from other chalcogenides both in crystalline structure and chemical behavior. Thus, one should expect markedly peculiar properties of nanoparticles in the Cd-Se-Te system as compared with those in the Cd-Se-S. So, the most stable crystalline structure of CdTe at room temperature is cubic (sphalerite), whereas the most stable phase for CdSe is hexagonal (wurtzite). Quantum-size effects in CdTe are more pronounced due to the larger value of exciton Bohr radius ($a_B = 7.5$ nm against $a_B = 5.4$ nm for CdSe) and the lower effective mass of electrons. All that supports importance to study CdTe nanoparticles.

We use a method of silicate glass activation leading to semiconductor nanoparticles formation different from the conventional oxide melting followed by chalcogenization ($\text{CdO} \rightarrow \text{CdS/Se}$). We elaborated conditions allowing a direct doping with chalcogenide precursor. The composition of the glass matrix used admits the noticeable solubility of cadmium chalcogenides and their solid solutions. Such method is more appropriate for production of glasses doped with complex

compounds, and we have succeeded in preparation of nanoparticles of the system Cu-In-S-Se [3] with controllable size and composition. The aim of the present work is to establish the pathways of $\text{CdSe}_x\text{Te}_{1-x}$ nanoparticles formation within the silicate glass matrix and determine their optical properties in dependence on solid solution composition and heat post-treatment.

2 Experimental

The glasses under study were prepared on the basis of the silicate system $\text{SiO}_2\text{-CaO-M}_2\text{O}$ ($\text{M}=\text{Li, Na, K}$). The undoped glasses have high optical transmission in the visible and near IR ranges. The temperature of synthesis was 1620 ± 10 K. Alkali composition of these glasses was adjusted for best dopants solubility and optical quality of the final samples. Crystalline compounds $\text{CdSe}_x\text{Te}_{1-x}$ were synthesized from elements and characterized with powder X-ray diffraction analysis. In the range of $0 < x < 0.2$ the solid solution had the CdTe-bulk like (sphalerite) lattice while the compound with $0.4 \leq x < 1$ demonstrated the wurtzite phase (CdSe-bulk like). Semiconductor dopants were introduced into the preparation batch in the amount of 0.75 wt.%, and activated carbon (2 wt.%) was added to prevent oxidation. Melts were rapidly cooled, and a part of the samples were annealed (under different temperatures lower than the softening, ~ 900 K) in air with subsequent slow cooling. Transmission electron microscopy (TEM) was carried out with an electron microscope UEMV-100LM by the method of "carbon replica with extraction" taken off from the as-etched glass samples. Optical spectra (spectrophotometers Specord M40 and CARY-17D) were recorded for polished samples of 0.25-0.5 mm thickness.

3 Results and discussion

Nanoparticles formed within the glass matrix are shown in Fig. 1 for a series of $\text{CdSe}_x\text{Te}_{1-x}$ solid solutions with various composition and for the post-heating at 550°C and 600°C . The micrographs indicate that nanoparticles have near-spherical shape, sometimes they are aggregated, the mean diameter is 10-20 nm. Also, the surface relief in areas close to particles shows inhomogeneous features created, perhaps, during cooling of the system due to different melting temperatures of the semiconductor and the glass (at least several hundreds of K).

The thermal treatment of the glasses results in growth of the particles only a little (Fig. 1), and their concentration remains practically unchanged. Therefore, the nucleation process is finished completely at the step of glass preparation. The subsequent heating produces no new particles. Perhaps, a creation of the prime particles prevented supersaturation in glass.

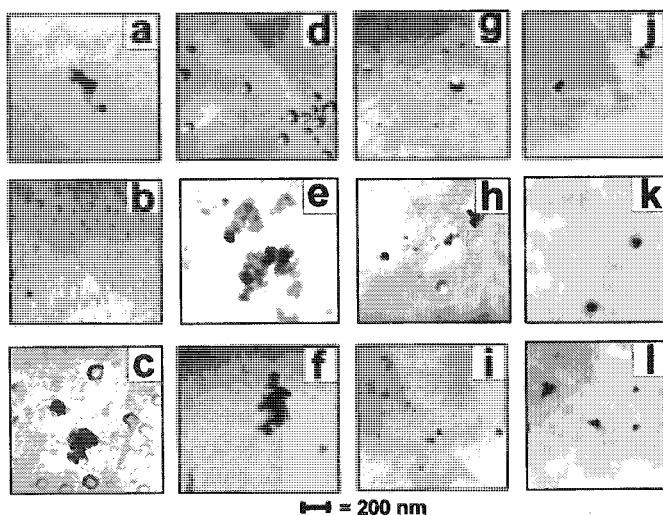


Figure 1. TEM micrographs of the glasses doped with $\text{CdSe}_x\text{Te}_{1-x}$ at various x : CdSe (a-c); $\text{CdSe}_{0.8}\text{Te}_{0.2}$ (d-f); $\text{CdSe}_x\text{Te}_{1-x}$ (g-i); $\text{CdSe}_x\text{Te}_{1-x}$ (j-l) and their changes as the result of heat treatment in air: 550°C (b,e,h,k) and 600°C (c,f,i,l). The micrographs of samples before heating – (a,d,g,j).

Absorption spectra of a series of glasses are presented in Fig. 2. A part of them are monotonously descending curves without any features (for the glasses with CdSe and Se-rich nanoparticles before the heat treatment), however the spectra for CdTe and the solid solutions after heating look as the pronounced maxima located in the range of 500-560 nm. A little red shift occurs under increase of the heating temperature (Fig. 2, $\text{CdSe}_{0.4}\text{Te}_{0.6}$). Evidently, the tendency of the maximum development is more featured for Te-containing nanoparticles, and the solid solutions show the maxima only after the heating. This feature can be associated with excitonic absorption in the nanoparticles similar to those observed earlier in CdTe quantum dots [1,4,5]. Such behavior in the maximum appearance is proposed to be explained by the transformation of crystalline phases in nanoparticles from wurtzite-like (initial for CdSe and Se-rich particles) to sphalerite-like (initial and heated CdTe and Te-containing ones). The appearance of this excitonic transitions in CdTe-like structures is more probable because CdTe has the larger Bohr excitonic radius (Section 1). The red shift does not correspond to the feasible growth of the particles, since this growth was not observed between 550°C and 600°C heating regimes (Fig. 1).

The hypothesis on the phase transformation under heating of $\text{CdSe}_x\text{Te}_{1-x}$ nanoparticles is consistent with the phase diagram of this system well known for the bulk compounds: this system includes the narrow two-phase region in which sphalerite and wurtzite $\text{CdSe}_x\text{Te}_{1-x}$ coexist at $0.8 < x < 0.5$ under temperatures above 800°C. This interval corresponds to our observed range of x values with the temperature stimulated appearance of the excitonic maximum.

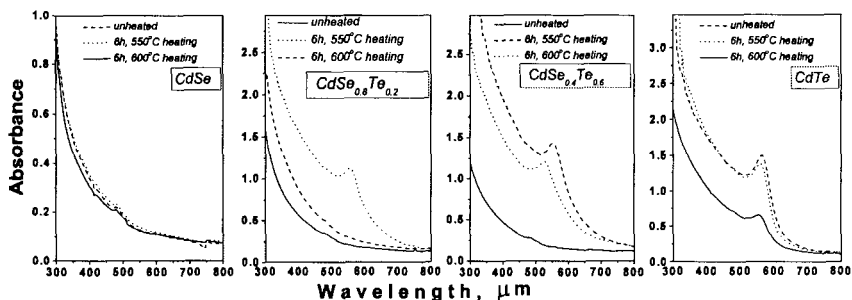


Figure 2. Absorption spectra of the glasses doped with $\text{CdSe}_x\text{Te}_{1-x}$ at various x (indicated) and their changes as a result of heat treatment in air.

4 Conclusion

Silicate glasses with $\text{CdSe}_x\text{Te}_{1-x}$ nanoparticles were fabricated by the method of direct doping that lead to formation of nanoparticles 10–20 nm in diameter at the first step of glass preparation. No additional particles were nucleated under subsequent heating. Optical absorption of CdTe- and other Te-containing nanoparticles is featured by excitonic maxima existing even in as-prepared CdTe-doped glasses, while $\text{CdSe}_{0.4}\text{Te}_{0.6}$ and $\text{CdSe}_{0.8}\text{Te}_{0.2}$ discover the maxima only after heating. The latter effect is associated with temperature-stimulated phase transformation from wurtzite lattice (CdSe, non-quantum sized particles) to sphalerite lattice (CdTe, weak quantization in the present case).

The work was carried out under support of Ministry of Education of Belarus.

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FORMATION AND OPTICAL PROPERTIES OF ULTRAFINE I-III-VI₂ PARTICLES IN SILICATE GLASS MATRICES

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Nanoparticles of ternary I-III-VI₂ semiconductor compounds were fabricated within three types of silicate glass matrices distinguished by alkali components. Their fundamental absorption edge depends on the chemical nature of semiconductor. CuInTe₂ and CuGaTe₂ particles are formed only in the multi-alkali matrix, while CuInS₂ is less sensitive to the matrix type.

1 Introduction

Solid state structures based on inorganic glasses and complex semiconductor compounds are of great interest among optical materials due to nontrivial physical properties of low-dimensional semiconductors fabricated within glasses as isolated quantum dots [1]. Their optical features originate from the nature of semiconductor, its proper absorption and variations provided by occurrence of the nanoparticles in a matrix. I-III-VI₂ semiconductors in glasses are rarely studied [e.g., 2,3], however chemistry of these compounds and variable optics open many promising applications through the wider spectral range than binary semiconductors. In the present work, we concern a series of copper-indium chalcogenides incorporated into glass matrix and present also preliminary data on copper-gallium telluride. The latter were fabricated in the glasses for the first time.

2 Experimental

We used two compositions for glass preparation differed only by content of alkali components: (SM1) SiO₂-CaO-Na₂O with 15.7 mol% of Na₂O, (SM2) with 22.0 mol% of Na₂O and (SM21) same as SM2 with equimolar substitution of Na₂O onto Li₂O-Na₂O-K₂O in ratio 1:1:1. The undoped glasses were colorless. Their proper absorption enters the UV range and begins from $\lambda=300$ nm. Crystalline compounds I-III-VI₂ were synthesized from elements and characterized with powder X-ray diffraction (XRD) analysis. A synthesis of glasses doped with the semiconductors was carried out in the reducing conditions (1670-1700 K) via melting of mixtures from the above components with powdered dopants [4]. Transmission electron microscopy (TEM) was carried out with an electron

microscope UEMV-100LM by the method of “carbon replica with extraction” taken off from the as-etched glass samples. Optical spectra (spectrophotometers Specord M40 and CARY-17D) were recorded for polished samples of 0.2-0.5 mm thickness.

3 Results and discussion

The synthesized doped glasses acquired specific color at the cooling step depending on the nature of semiconductor and its concentration. We have succeeded in fabrication of the glasses with dopant concentration up to 0.75 wt% that was quite sufficient for an appropriate optical absorption of samples with thickness of tenths of millimeters. An increase of dopant concentration in the case of tellurides was difficult because of their lower solubility.

TEM results directly evidence on appearance of nanoparticles together with specific relief of the matrix in the particle surrounding. Diameter of the particles varies in the range of 20-100 nm. Nanoparticles are usually located in the specific cavities those can appear due to very different melting temperatures of matrix and semiconductors ($\Delta T > 300$ K).

It should be noticed that a direct confirmation of the nanoparticles composition is possible for materials of this type only in some special cases, when amount of dopants is rather high. The glasses under consideration do not reveal any XRD pattern of crystalline phase, and we may not exclude a partial change in stoichiometry of the compounds and creation of structure defects in the nanocrystals.

A series of transmission spectra is given in Fig. 1 for the glasses doped with 0.75 wt% of the different semiconductors. Change of the matrix composition, which consists only in variation of alkali components, is shown to influence very strongly upon the spectra. SM1 (only Na_2O as alkali component) appears to be very selective to formation of transparent I-III-VI₂ semiconductor-doped glasses (Fig. 1a). Very low transparency for CuInTe_2 - and CuGaTe_2 -doped materials can be associated with complete decomposition of the compounds and formation of some metal-like phase.

SM2, that includes just somewhat more sodium oxide, reveals the similar results (Fig. 1b). Only small amount of CuInTe_2 and CuGaTe_2 produces nanoparticles coloring the glasses: the weakly noticeable absorption edge of about $1\ \mu\text{m}$ occurs, but the whole transparency is very low. The other couple of compounds, CuInS_2 and CuInSe_2 , can produce the doped glasses with both SM1 and SM2. Moreover, the second matrix can be characterized as more optimal to attain the sharp absorption edge, and the difference in E_g of the sulfide and selenide within it is minimum. In the glass SM1 this difference in E_g fits more in correspondence with E_g values of CuInS_2 and CuInSe_2 ($\Delta E_g \sim 0.2\ \text{eV}$) [5].

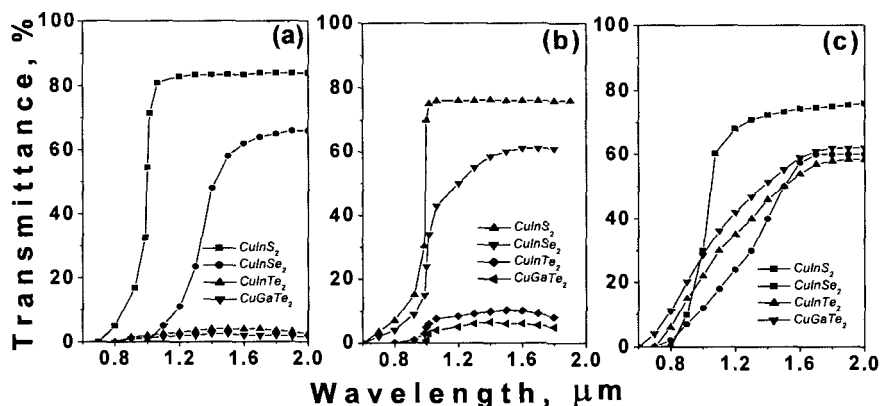


Figure 1. Absorption spectra of the glasses doped with different ternary compounds (indicated) for the three glass matrices used: (a) SM1; (b) SM2; (c) SM21.

The matrix with multi-alkali composition, SM21 (Fig. 1c), shows very different behavior with respect to formation of the nanoparticle-doped glasses with CuInTe_2 and CuGaTe_2 ; the spectra are similar to those with CuInSe_2 . Also, we observe the noticeable tail in the visible range ($\lambda < 0.8 \mu\text{m}$) for these compounds that can be associated with additional absorption above E_g , likely, due to contribution of indirect transitions. CuInS_2 nanoparticles in SM21 matrix indicate the spectrum almost identical to those in another matrix. However, CuInSe_2 acquires also the weak absorption band peaked about $\lambda = 1.2 \mu\text{m}$. Thus, one can conclude that CuInS_2 nanoparticles are easily formed in silicate glass matrices of different compositions. Their semiconductor properties depend little on the matrix. Within the series of CuInX_2 compounds, where $X = \text{S, Se, Te}$, this effect becomes more evident revealing an increase of chemical reactivity.

The doped-glasses under study were tested also with respect to annealing at temperatures up to 650°C (the maximum admissible for these glass compositions to avoid softening and melting). Such annealing is conventional in glass technology to initiate particle nucleation and growth. However, we did not observe essential changes for all the compounds. Hence, the completion of nucleation step occurs at the first melting-cooling operation in our case. This mechanism can explain the pronounced effect of the glass matrix composition upon feasibility of compounds to form nanoparticles and their final properties. The matrix in a melt plays the role of active medium providing stability of these complicated compounds.

4 Conclusion

A series of silicate glass matrices which were different in nature and concentration of alkali components were used for preparation of the semiconductor-doped glasses

with ternary compounds: CuInS_2 , CuInSe_2 , CuInTe_2 and CuGaTe_2 . The direct doping of the glass-forming oxide mixtures with the semiconductor compounds resulted in formation of nanoparticles with diameter of tens of nanometers. Optical spectroscopy in the range of the fundamental absorption edge of the compounds showed that CuInS_2 and CuInSe_2 nanoparticles can be formed in three matrices, while only the multi-alkali composition provides formation of CuInTe_2 and CuGaTe_2 particles. The matrix has also the noticeable effect upon E_g of the nanoparticles. The results considered are of interest for manufacturing of new optical glasses with broad class of ternary compounds.

Acknowledgements

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STRUCTURE EVOLUTION DURING LASER SINTERING OF FINE POWDERS

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The structure evolution in the course of laser sintering of fine SiO₂ powder is studied experimentally. A specific correlation between different types of pores and the rate of the pore reduction during sintering is revealed.

1 Introduction

Laser sintering of powders is an effective technique for creation materials with improved properties [1]. Recently it was shown an expediency of laser sintering application to nanostructured materials [2,3]. It should be noted that on the whole the level of comprehension of nanopowder sintering mechanisms by laser radiation is rather low. On the one side, the nanoparticles are susceptible to sintering due to greatly reduced melting point. Besides, they possess a high ability for aggregation. Therefore, the nanopowder sintering is characterized by the pronounced coalescence and local isolation of particles. On the other side, the laser sintering is a short time process. Therefore, due to the short period of laser beam action it is possible to prevent or limit recrystallization processes and, as a consequence, to retain the nanostructure of the sintered material. Thus, it is necessary to strongly adjust the energy and time parameters of laser sintering in order to achieve the required result of the process.

The aim of this paper is to study the evolution of structure in the course of laser sintering of fine SiO₂ powder. It should be noted that there are some technical difficulties in the study of sintering kinetics in case of traditional powder technology when the long time furnace sintering is used. It is especially difficult to carry out the study using such technique in the case of nanopowders.

In the paper, a specific approach to investigation of sintering kinetics was proposed. The experiments on laser sintering were carried out with the use of a number of testing samples. The duration of laser processing, τ , was varied for different samples. This allowed to elucidate important features of structural evolution at different stages of the sintering process.

2 Experimental

Pure SiO₂ powder (particles of spherical shape of 300-400 nm in size) was used in the study. The temperature of softening and melting of SiO₂ is favorable for laser sintering as a result of surface melting, rearrangement and accommodation. Tape-like specimens of 230 μm thick were fabricated by sol-gel technology. CW-CO₂ laser ($\lambda = 10.6 \mu\text{m}$, $Q = 100 \text{ Wt/cm}^2$) was used for sintering. The choice of this laser is explained by high absorptance of SiO₂ (0.96) for radiation with $\lambda = 10.6 \mu\text{m}$ [4]. Scanning electron microscopy was used for the structure characterization. A mean particle size and mean pore size were estimated from fractured surfaces, as well as average porosity, which was defined from the ratio of pore surface to the total one.

3 Results and discussion

In the initial powder compacts, the particles were non-uniformly distributed over the volume (the pronounced inhomogeneity of density took place). As a rule, the particles were united to the comparatively large aggregates of 5-10 μm in size that involved the mean aggregates of 2-3 μm in size. Besides, there were both large and average aggregates containing small aggregates of about 1 μm in size. Initially it was possible to observe the following types of pores: (1) large pores of about 3 μm in size (between the large aggregates), (2) mean pores of about 1 μm in size (between the mean aggregates), (3) small pores of about 0.05 μm in size (between the particles with the defects in their packing) and the smallest pores of about 0.02 μm in size (between the particles without defects in their packing).

This complicated multi-level local isolation of particles in the initial powder compacts influenced the structure evolution during sintering that was accompanied by the increasing the particles (aggregates) in size and decreasing the pores in both quantity and size. In particular, the unexpected phenomenon that is the correlation between the pores' types mentioned above and the rate of decreasing the pores in quantity and size was revealed (Figs. 1,2).

The smallest pores disappeared in 3-5 s, the small pores – in 7-9 s and large pores – in 14-16 s after the laser processing start and only average pores retained during all periods of processing (they decreased in size down to ~ 0.5 μm in 8-10 s after the processing start and then their size was constant). The quantity of pores of different types was decreased by similar way. As a result, the pores of different types made the certain contribution to the total porosity change. In particular, the total porosity decreased from 40% to 5% while the porosity caused by the smallest, small and large pores decreased correspondingly from ~ 23%, ~ 5% and ~ 2% to 0 and the porosity caused by mean pores decreased from ~ 10% to ~ 5%.

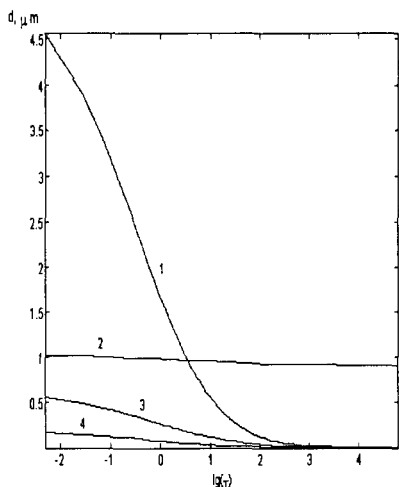


Figure 1. Pores' size d as a function of laser processing time τ (s).

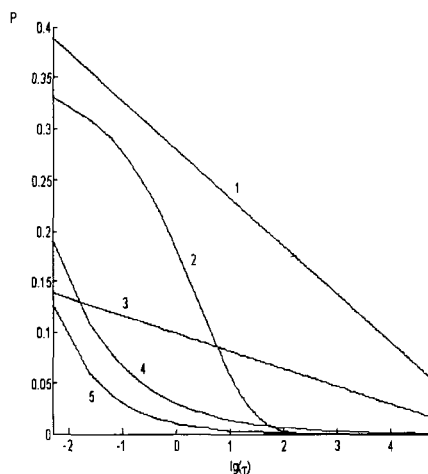


Figure 2. Porosity P as a function of laser processing time τ (s).

The reason of intensive local isolation of particles during sintering is a large difference between local and integral shrinking rates. In the case of laser sintering the high local isolation rate is conditioned by surface melting of particles and their rearrangement controlled by viscous flow under capillary forces.

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PECULIARITIES OF ELECTROCHEMICAL SYNTHESIS OF NANOSIZED SiO₂ FILMS

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The conditions of low-temperature nano-sized SiO₂ film synthesis in electrochemical treatment of silicon have been investigated. The influence of physicochemical properties of the electrolyte and single-crystal silicon and of the conditions of rapid thermal annealing has been examined.

1 Introduction

The tendency of electronic industry to nanotechnologies requires formation of individual elements in integrated circuits (ICs) [1]. To date the most commonly encountered insulator-semiconductor structure continues to be Si/SiO₂ system where the oxide films on the surface of single-crystal silicon are formed, preferentially, by high-temperature oxidation. But the strategy of decreasing IC components sizes limits the opportunities of this method because the growth time of SiO₂ layers under high temperatures decreases as their thickness is reduced. Therefore, the formation of nano-sized oxide-silicon films takes place under the growth conditions in the initial stage. In this connection, it is extremely difficult to control the given process. The synthesized dielectric layers exhibit high nonuniformity in thickness and properties over silicon substrate [2].

The electrochemical oxidation of silicon is of interest for the formation of ultrathin dielectric layers due to its low temperatures and easy controllability of the process [3]. In this case, the efficiency of the electrochemical treatment of the materials when oxide layers of low thicknesses are synthesized on their surfaces depends on the uniformity of the charge distribution at the solid phase/electrolyte interface. A great impact on this factor is made by adsorption processes, particularly, chemisorption ones, but their role in the formation of nano-sized films is, not yet understood.

In this paper we examine the conditions of 4-15 nm thick oxide layers synthesis against the physicochemical properties of the electrochemical system (solvents, current-conducting additives of the electrolyte, silicon anode) and their roles in chemisorption processes.

2 Method

The anodic treatment process was carried out in a combined regime: first, galvanostatically at a current density of 1 mA/cm^2 up to the formation voltages (U_{form}) of 10-50 V, and then, when the given U_{form} was reached, potentiostatically, up to the current of 0.01-0.02 mA. To measure characteristics of the anodically oxidized silicon (AOS) (thickness, dielectric properties, and their surface distribution) the anodic treatment of the silicon wafers was done in a cell with the anodization area of 5 cm^2 . Single-crystal boron-doped (100) silicon wafers of resistivity 0.3 Ohm-cm, phosphorus-doped (100) and (111) silicon substrates of resistivities 0.1 and 4.5 Ohm-cm, respectively, and boron-doped (100) and (111) silicon wafers of resistivity 4.5 Ohm-cm were used as silicon anodes.

The electrolytes were prepared using water, ethyl alcohol, ethyleneglycol, dimethylformamide as solvents of the current-conducting additives. The current-conducting additives were: tartaric acid, potassium nitrate, ammonium nitrate and aluminum nitrate. The thicknesses of the synthesized AOS films were measured by laser ellipsometer in 5 points on the surface. Their dielectric characteristics were estimated from C-V curves also in 5 points.

3 Experimental results and discussion

Table 1 presents characteristics of the solvents used along with the dielectric properties of the synthesized AOS. Tartaric acid was used as a current-conducting additive in this case. Its concentration was 1 mol/l. The initial voltage in all the electrolytes was 5-7 V. The anodic treatment of boron-doped, 0.3 Ohm-cm – silicon wafers was performed up to $U_{\text{form}}=20 \text{ V}$. This allowed the AOS layers of $10 \pm 0.2 \text{ nm}$ thick to be synthesized.

Table 1. Characteristics of the solvent molecules [4] and AOS dielectric strength.

Solvent	Molecular weight	Dipole moment, M	Dielectric constant, ϵ ($^{\circ}\text{C}$)	Donor number DN	Surface tension, G, dyn/cm	Dielectric strength U, $\text{V/cm} \cdot 10^{-8}$
Water	18	1.84	80.4 (20)	18.0	72.8	48.0 ± 13.6
Ethylalcohol	46	1.69	24.3 (25)	16.4	22.1	37.2 ± 10
Ethylene-glycol	62	1.50-2.20	37.7 (25)	17.1	46.0	18.4 ± 2.1
Dimethyl-formamide	73	3.82	36.7 (25)	26.6	36.7	39.7 ± 2.0

The AOS layers synthesized in an aqueous electrolyte have the highest dielectric strength. But these coatings also feature the highest spread in values of

this characteristic over the anode surface. It bears witness to high heterogeneity of the oxide chemical composition and oxygen-silicon network.

In the electrolytes prepared with the use of such solvents as ethyl alcohol and ethyleneglycol, both the AOS layer dielectric strength and the spread in values of this characteristic over the anode surface are reduced. The increase of the solvent molecular mass here brings about the decrease in the AOS dielectric strength. The Table 1 data also indicate that the solvent molecules asymmetry characterized by the dipole moments (these characteristics of the first three solvents are close to one another) takes an insignificant part in the total effect of the electrolyte on the formation of the nano-sized AOS layers. But the used solvents (Table 1) differ in their molecules, molar weight (their mobilities), in dielectric constants and surface tensions. Since the mentioned characteristics of the solvent molecules influence the thickness of the diffuse portion of the double electric layer at the solid/solution interface [5], this, in its turn, affects the AOS charge distribution at the Si/electrolyte interface and, hence, the synthesis of the nano-sized SiO_2 layers. Specifically, water has the highest dielectric constant and surface tension. Its molecules are characterized by high mobility. As a result, the thickness of the diffuse portion in this electrolyte will be the smallest. It leads to a sharp drop in the charge amount in the Si/electrolyte system causing the formation of the SiO_2 layers whose dielectric properties demonstrate high nonuniformity (Table 1).

Dimethylformamide stands out from the other solvents in the group. The AOS films synthesized in an electrolyte based on it demonstrate a relatively uniform dielectric properties over the anode surface. The molecules of this solvent have the largest donor number suggesting their enhanced capabilities to take part in the electron transfer to the groups with uncompensated bonds which form on the silicon anode surface. The adsorption of such molecules on the solid surface is likely to be assigned to chemisorption.

The investigation of the nano-sized AOS synthesis on phosphorus-doped, 0.1 Ohm-cm wafers, phosphorus-doped, 4.5 Ohm-cm wafers and boron-doped, 4.5 Ohm-cm silicon substrates in an ethyleneglycol electrolyte containing water and tartaric acid has elucidated the fact that an increase in resistivity of single-crystal silicon, its conductivity type and crystallographic orientation all have nothing to do with the growth rate of such films. But their dielectric strength values are nearly 1.3 times higher if the films are formed on silicon wafers of higher resistivity. It suggests that the formation of anodic nano-sized SiO_2 layers should be predetermined by the density of the natural oxide film on the silicon surface. Comparing this data with the one presented above, it may be concluded that the main potential-determining reaction in the formation of nano-sized AOS is electrochemical adsorption which favours the electrons transfer and the generation of negatively charged oxygen-containing groups on the silicon wafer surface which migrate to the AOS/Si interface. An introduction of water or dimethylformamide seems to accelerate their formation at the expense of the chemisorption energy.

To examine the possibility of a practical use of nano-sized AOS in ICs, we have investigated annealing of these films both in inert and oxygen-containing atmospheres over the temperature range of 300-1200°C. It has been found that annealing of such films in the temperature range of 400-500°C for 0.5 min enhances their dielectric strength by a factor of 5 with no change in thickness of the oxide layer. The most favourable atmosphere for the annealing is an oxygen-containing one. At the anneal temperatures of more than 500°C, the initial AOS thickness increases nearly twofold, and the dielectric characteristics of these films show a nonuniform distribution over the surfaces.

In summary, the whole cycle of the investigations carried out allows us to suggest that electrochemical anodic structuring of the natural oxide coating on the single-crystal silicon in the electrolytes of a given composition combined with the rapid low-temperature annealing makes possible the formation of dielectrically strong AOS layers for nano-sized IC structures.

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INORGANIC PARTICLES FORMATION IN NANOENGINEERED POLYMER CAPSULES

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Inorganic synthesis inside restricted volume of micron-scale poly(styrene sulfonate)/poly(allylamine hydrochloride) capsules is described. Inner inorganic layer comprised of magnetic nanoparticles (Fe_3O_4 , CoFe_2O_4 , MnFe_2O_4 , ZnFe_2O_4), rare earth fluorides, hydroxyapatites or metal nanoparticles (Ag) was precipitated exclusively inside polyelectrolyte capsules forming the mechanically stable hollow inorganic shell. Synthesized inorganic nanophase was characterized by TEM, SEM, and WAXS techniques. The phase consists of weakly-crystallized particles of 5-9 nm bounded to each other by polyelectrolyte molecules. Polyelectrolyte capsules loaded with ferrite (magnetite) particles are magnetically active enough for manipulating them in a water solution by an external magnetic field.

1 Introduction

Micron and submicron sized polyelectrolyte capsules having nano-engineered wall made of polyelectrolyte multilayers were recently introduced [1]. These hollow shells were made by means of layer-by-layer adsorption of oppositely charged polyelectrolytes (poly(styrene sulfonate)/poly(allylamine hydrochloride, etc.) [2] on the surface of colloidal template core (SiO_2 , MnCO_3 , melamine formaldehyde, etc.) followed by dissolution of the latter in an acidic media. Polyelectrolyte shell can be formed from different substances: synthetic and natural polyelectrolytes, proteins, nucleic acids, inorganic nanoparticles, dyes and lipids [3]. Polyelectrolyte capsules can also act as microcontainers for a wide range of materials: polyelectrolytes, dyes, inorganic particles, and quantum dot nanoparticles [4,5]. In particular, positively charged polyelectrolytes captured inside capsules arise pH-gradient across the capsule shell [4] that is necessary for charge compensation of different anions, which can be further involved in spatially restricted chemical reactions. Here we present a general idea for inorganic synthesis in micron-scale volume of polyelectrolyte capsules.

2 Experimental

Initial poly(styrene sulfonate) (PSS, MW ~ 70000) / poly(allylamine hydrochloride) (PAH, MW ~ 50000) polyelectrolyte capsules containing 0.1 M of PAH monomers

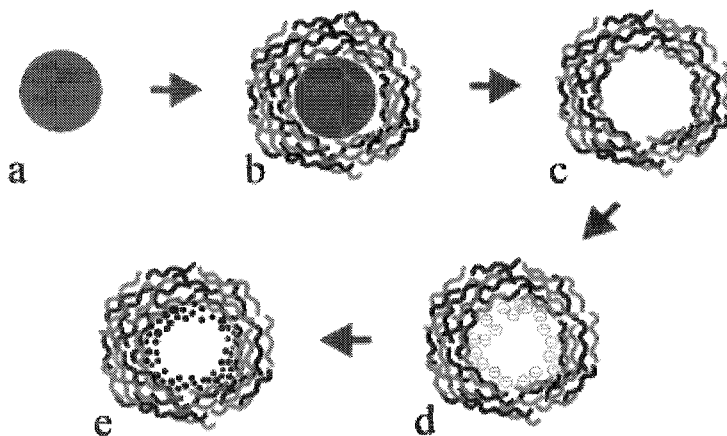


Figure 1. Schematic illustration of hollow polyelectrolyte capsule formation (a-c) followed by the selective inorganic synthesis inside (d-e). a-b: layer-by-layer precipitation of poly(styrene sulfonate), poly(allylamine hydrochloride) monolayers; b-c: dissolution of template core; c-d: loading of polyelectrolyte capsules with corresponding anions; d-e: precipitation of inorganic material from corresponding salts.

inside were used as microreactors for synthesis. Capsules were formed by controlled precipitation of PAH complex with citric acid on the weakly cross-linked melamine formaldehyde or MnCO_3 template particles (diameter 3–5 μm) with sequential assembling three PAH/PSS multilayers on the top of the core/PAH particles using layer-by-layer technique (Fig. 1). Template core was removed in HCl solution at $\text{pH}=1$.

Before inorganic synthesis, loading of PAH/PSS polyelectrolyte capsules with corresponding counter anions (OH^- , F^- , PO_4^{3-}) was made as follows: PAH/PSS capsules (5 %v/v) were immersed in 0.01 M NaOH (for ferrites and magnetite formation), 0.1 M HF (for YF_3 synthesis) or 0.1 M H_3PO_4 (for hydroxyapatite synthesis) for 24 h (Fig. 1c-d). After washing anion-loaded polyelectrolyte capsules were ready for inorganic precipitation.

3 Results and discussion

Adding (OH^- , F^- or PO_4^{3-})-containing capsules to the aqueous solution of metal cations ($\text{Fe}^{2+}/\text{Fe}^{3+}$, Y^{3+} or Ca^{2+} , respectively) leads to the formation of inorganic nanoparticles only inside the capsules without any traces of precipitate in the surrounding medium. As observed with WAXS technique, precipitated Fe_3O_4 , YF_3 or hydroxyapatite are weakly crystallized with traces of corresponding hydroxides ($\text{Fe}(\text{OH})_3$, $\text{Y}(\text{OH})_3$). Formation of the latter can be explained by hydrolysis of metal cations in the presence of PAH molecules which increase pH inside the capsule volume. Crystallite size, estimated from the broadening of XRD peaks varies within the range of 8–10 nm. SEM images of polyelectrolyte capsules filled with inorganic

precipitate (Fig. 2) demonstrate the spherical-like morphology similar to the original one for the polyelectrolyte capsule in the solution. It is necessary to emphasize that inorganic scaffold inside polyelectrolyte capsules prevents their collapse upon drying, which is typical for empty polyelectrolyte capsules. Moreover, as seen in Fig. 2, part of the polyelectrolyte shell was exfoliated exhibiting the inner inorganic layer. As shown on TEM image of magnetite-loaded PAH/PSS capsules (Fig. 2d), the deposition of the inorganic material occurs presumably on the inner PAH/PSS wall and resulting dried polyelectrolyte/inorganic composite capsules appear to be hollow.

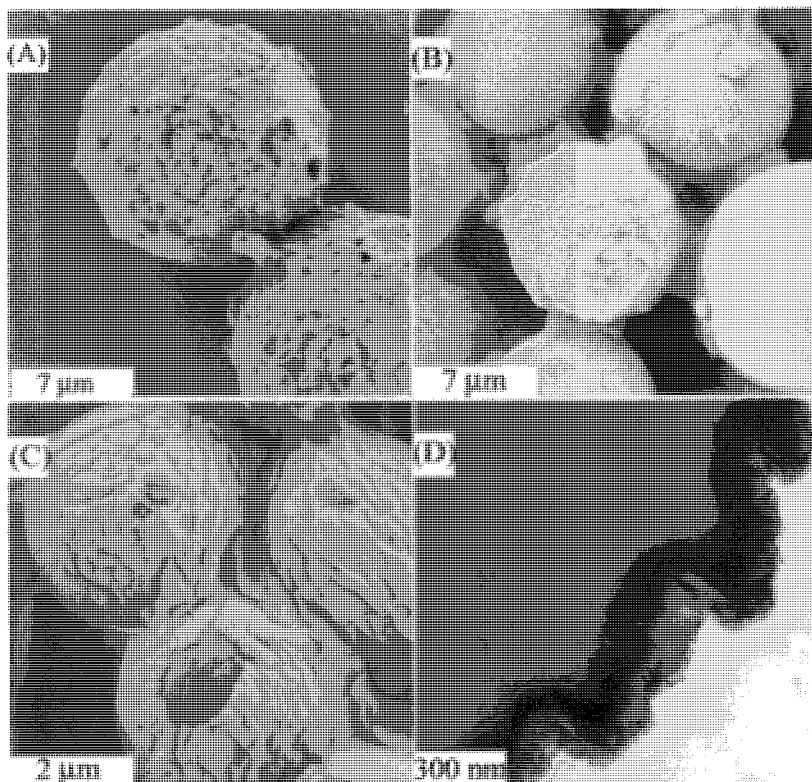


Figure 2. SEM images of polyelectrolyte capsules filled hydroxiapatite (a), Fe₃O₄ (b) and YF₃ (c). (d) – TEM image of ultramicrotomed polyelectrolyte capsule filled with Fe₃O₄.

4 Conclusion

In conclusion, controllable inorganic precipitation can be performed exclusively inside polyelectrolyte capsules forming the hollow composite structure. Capsules bearing material with certain properties (conductivity, magnetic susceptibility, etc.) can find practical applications in novel micron-scale electronic and optoelectronic devices, drug delivery, microreactors for spatially restricted catalytic chemical and biochemical synthesis. The influence of micron-scale volume and capsule composition on chemical reactions in capsule interior is a subject for further investigations.

Acknowledgements

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NANOCRYSTALLINE PEROVSKITE-LIKE Sr–Ba–Fe–Co OXIDES: STABILITY UNDER REDUCING CONDITIONS

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Stability of nanocrystalline powder samples, synthesized in Sr–Ba–Fe–Co–O system by the mechanochemical activation route in H_2 atmosphere is investigated. Samples of various compositions were used to establish the main reasons of samples destruction. XRD, EPR and XPS methods were employed to characterize the samples before and after treatment in the H_2 atmosphere (600 °C, 1 h). Essential content of cobalt in a sample was found to degrade its stability, whereas an insertion of additional amount of Fe_2O_3 at the end of the mechanochemical activation enhances stability.

1 Introduction

Perovskite-like Fe(Co) containing oxides have attracted research interest because they are considered as promising materials for preparing membrane catalysts used to produce syngas ($CO + H_2$) by direct conversion of methane and other basic hydrocarbon gases using the oxygen of air [1]. The use of oxides with nanosized grains is perspective because it allows to produce ceramics of required density and conductivity. The mechanochemical approach admits easily to synthesize complex nanoscaled oxides. It is very important that samples, prepared by the mechanochemical activation method, are composed of nanosized domains with defect structure separated by amorphous matter. These features provide such properties of the membranes as high electronic and O^{2-} conductivity due to high density of intergrain boundaries and superplasticity.

One of the main problems encountered in this application is a degradation of solid conductors in reducing atmosphere of reaction products (CO, H_2). The present work is devoted to some aspects of this problem. The aim of the research was to establish main reasons responsible for degradation of perovskite-like Sr(Ba)–Fe–Co–O complex oxides under reducing conditions, and to find the most stable sample among those providing high electronic and O^{2-} conductivity. For this purpose we studied some physico-chemical characteristics of mentioned above samples before and after thermal treating in H_2 atmosphere, by using XRD, EPR and XPS methods.

2 Experimental

The starting reagents were SrCO_3 , BaCO_3 , Fe_2O_3 and CoO . Complex oxides in Sr–Ba–Fe–Co–system were prepared by 5 min mechanical milling of the starting compounds blends in AGO planetary mill (steel balls) followed by calcinations at 1000–1100°C. To decrease the iron contamination and to increase the activated mixture homogeneity, a proprietary procedure of mechanochemical treatment was used. The milling and firing procedures were three times repeated, and then samples were once again milled for 10 min. In some cases additional amount of Fe_2O_3 was added at the final stage of the mechanochemical treatment.

Reduction in H_2 atmosphere was performed in the following manner: system was heated up to 600°C during 1 h, kept at this temperature for 1 h and then cooled to room temperature during 0.5 h.

X-ray powder diffraction data (XRD) of the samples were obtained with HZG 4A powder diffractometer (CoK_α radiation, MnO_2 filter). EPR spectra were recorded at 77 K and 300 K in X-band range, by using VARIAN E112 spectrometer. The g values were determined using DPPH as a standard. XPS studies were performed with ES 2401 spectrometer. Sample surface etching with Ar^+ was employed. Core level energies were calibrated by the C 1s line with $E_B = 284.6$ eV.

3 Results and discussion

Prepared perovskite-like samples were different in molar ratio of Fe/Co and Sr/Ba. Only such samples were chosen for further analysis which revealed high electronic and O^{2-} conductivity and also provide high density of the ceramic material. Their compositions are presented in Table 1.

Table 1. Composition of the analyzed samples and XRD data of main phases.

Sample No.	Composition	Perovskite-like phase	
		Cubic unit cell dimension, Å	Grain size, nm
1	$\text{Sr}_3\text{BaFe}_3\text{CoO}_x$	3.874(2)	15
2	$\text{Sr}_{3.5}\text{Ba}_{0.5}\text{Fe}_{2.5}\text{Co}_{1.5}\text{O}_x$	3.873(1)	20
3	$\text{Sr}_4\text{FeCo}_3\text{O}_x$	3.874(2)	20
4	$\text{Sr}_4\text{Fe}_2\text{Co}_2\text{O}_x + \text{Fe}_2\text{O}_3^*$	3.895(1)	30

* Additional Fe_2O_3 was added at the final stage of the mechanochemical treatment.

Main crystalline phase of the prepared samples is perovskite-type solid solution. Whereas sample 2 is a single-phase, the remainder samples are multi-phases: samples 3 and 4 contain SrCO_3 as additional phase while sample 1 includes some amount of hexagonal $(\text{Sr},\text{Ba})(\text{Fe},\text{Co})\text{O}_x$. It should be noted that all the samples contain also amorphous matter. As follows from TEM data, two size ranges of particles are presented in the samples, 10–15 nm and over 300 nm.

There are some difficulties of the identification of crystalline phases for the samples after reduction, by using XRD data. Moreover, it is very important to know not only phase composition of crystalline part of the samples but also oxidation states of iron and cobalt. In view of these circumstances the investigations of EPR and XPS spectra of the samples before and after their reduction in H_2 atmosphere were performed to detect main features of degradation.

In the EPR spectra a weak signal at $g = 4.3$ is detected for all samples. In the samples 2–4 a broad line at $g \approx 2.0$ is also observed, which is essentially more intensive for the sample 4 in comparison with that for the samples 2 and 3. The signal at $g = 4.3$ in iron-containing oxide systems is related, as a rule, to Fe^{3+} ions located in strong crystal field. Because no EPR signals are appeared for perovskite-like $SrFeO_{3-\lambda}$, it may be supposed that the signal at $g = 4.3$ is caused by substitution of a part of Fe^{3+} ions by Co^{3+} . Signal $g = 4.3$ is caused by $(Fe^{3+}-V_O)$ defects in $Sr(Ba)Fe(Co)O_{3-\lambda}$. The broad line at $g \approx 2.0$ is indicative of amorphous or pseudoamorphous (crystalline phase of high dispersity) Fe_2O_3 . $(FeO_5)_2$ associates may be responsible for presence of this signal. From its intensity one may conclude that content of amorphous Fe_2O_3 in the sample 4 is essentially higher than that in the samples 2 and 3, and it is absent at all in the sample 1.

Presence of amorphous Fe_2O_3 in the samples enhances their stability. So, EPR spectra of the sample 4 before and after thermal treatment in H_2 atmosphere are very similar, what corresponds to only slight changes in the sample. In contrast, for the samples 1–3 the signals at $g = 4.3$ disappeared and ones at $g \approx 2.0$ were essentially broadened ($\Delta B = 250$ mT) after the reduction procedure. These data correlate with content of amorphous Fe_2O_3 in the samples. Moreover, as follows from XRD data, the samples 2 and 3, being treated in H_2 atmosphere, contains metallic cobalt (in the case of sample 3 its amount is essentially more as compared with the sample 2). This allows to conclude that essential cobalt content degrades its stability giving rise to metallic cobalt as a result of a reduction process.

Table 2 presents some XPS results of the sample 3, which was found to reveal the lowest stability. Three types of O^{2-} are presented in both initial and reduced samples 3, what are due to different extent of covalence for metal–oxygen bonds in the samples. $Fe\ 2p_{3/2}$ and $Co\ 2p_{3/2}$ lines reveal a complex structure what is caused by state uniformity of Fe and Co, and also by presence of XPS line satellites. It may be uniquely stated that cobalt and iron are present in a number of oxidation states in both initial and reduced samples 3. The reduction procedure causes more changes of $Co\ 2p_{3/2}$ core levels in comparison with $Fe\ 2p_{3/2}$ ones, because it gives rise to appearance of line with $E_B = 777.5$ eV belonging to Co^0 oxidation state. These data are in agreement with detection of metallic cobalt from XRD data.

Table 2. XPS data for the sample 3.

State of the sample	E_B , eV			
	O 1s	Sr $3d_{5/2}$	Co $2p_{3/2}$ *	Fe $2p_{3/2}$ *
Before reduction	530.7	133.2	779.0	710.1
	531.8		780.8	711.5
	532.8		782.3	712.2
				713.5
After reduction	530.0	133.1	777.5	710.0
	532.1		779.8	712.4
	533.5		781.7	714.2

* Line satellites are not given.

4 Conclusion

Essential content of cobalt in the mixed-oxide Sr–Ba–Fe–Co–O system degrades its stability in reducing atmosphere, giving rise to sample destruction because of Co^{n+} reduction (metallic cobalt may be a product of this process). Insertion of additional amount of Fe_2O_3 at the end of the mechanochemical activation enhances stability of the sample, because it favors formation of amorphous layers preventing destruction.

Acknowledgements

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SYNTHESIS AND BEHAVIOR OF MONOMOLECULAR FILMS FROM 2,4-HENEICOSANEDIONE AND ITS METALLOCOMPLEX

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An attempt to obtain a copper complex from 2,4-heneicosanedione directly on ionic subphase was undertaken. The properties of 2,4-heneicosanedione and its copper complex are investigated by π -A isotherms at water subphase. Incorporation of metal atoms into 2,4-heneicosanedione monolayer with chelate metallocomplex formation on ionic subphase has been proved by IR- and UV-spectroscopies. Stability of monolayer film depending on AFM tip effect or water presence was studied.

1 Introduction

Composite organic-inorganic Langmuir-Blodgett (LB)-films have unique properties due to a high degree of ordering [1-6]. A presence of metal atoms in the polar part of amphiphilic molecules can improve monolayer stability on a solid surface. Traditionally, metal is included in a monomolecular film in the form of an appropriate fatty acid salt (stearic, behenic, arachidic), or as pre-synthesized metalloorganic complexes (porphyrin, phthalocyanine). Recently, the works on formation of LB-films from 1,3-diketone metallocomplexes have been published [6]. Amphiphiles represent chemically synthesized complex of metal with 1,3-diketone from which the film will be formed subsequently. It seemed perspective to obtain 1,3-dicarbonylic metallocomplexes directly during monolayer formation at ionic subphase. The goal of the present work is to reveal such amphiphilic 1,3-diketones, which would be able to produce complexes with metal ions either on ionic subphase or in contact with metal surface.

2 Experimental part

The objects of our research were monolayer films formed on the base of 2,4-heneicosanedione (HD) and its copper complex $(HD)_2Cu$ on a water subphase. HD (Fig. 1a) was synthesized in accordance with [7]. Its copper complex, $((HD)_2Cu$, Fig. 1b) was obtained either via extraction reaction of Cu^{2+} ions (from cooper(II) acetate) with HD or by reaction between HD molecules and Cu^{2+} ions at

ionic subphase. Y-type bilayers were transferred to the substrate by the traditional vertical deposition method. Z-type monolayers were also formed by the "horizontal precipitation" (HP) method [8]. The surface pressure during the deposition was kept at 30 mN/m.

Silicon wafers were hydrophilized by heating in $\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ mixture (7:4:1, in volume) at 320 K. Such hydrophilic surface was either right away used for modification with LB film or first hydrophobized with octadecyltrichlorosilane (OTS) in $\text{C}_{16}\text{H}_{34}:\text{CCl}_4$ (4:1, in volume) solution.

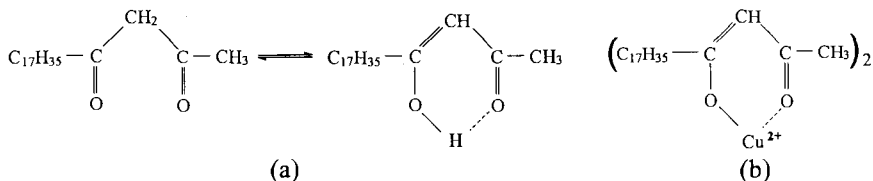


Figure 1. Chemical structures of HD (a) and $(\text{HD})_2\text{Cu}$ (b).

An automated Langmuir trough was used for measurements of surface pressure-area per molecule (π -A) isotherms and film deposition. The isotherms were recorded at a compression speed of $0.2\text{--}0.3 \text{ \AA}^2/(\text{molecule} \times \text{min})$. AFM images were obtained with a Nanoscope IIIa (Digital Instruments, USA) operated in the constant force mode (1–10 nN).

3 Results and discussion

The compounds under study are 1,3-diketone's derivatives and possess keto-enol tautomerism (Fig. 1). Besides, at certain conditions the replacement of "enol-hydrogen" by metal ions and formation of 1,3-diketone's metallocomplexes is possible. These compounds are amphiphiles and can form monomolecular films, that is confirmed by the pressure (π)-area (A) isotherms (Fig. 2). It was assumed that copper ions to be included in HD-film occurred on ionic subphase. This conclusion was done comparing the minimal area per molecule A_0 for the films of HD (1) and $(\text{HD})_2\text{Cu}$ (2) on water subphase, and for HD film on ionic subphase (3) ($A_0(1) < A_0(3) < A_0(2)$). Moreover, it also was established that $(\text{HD})_2\text{Cu}$ forms a solid film on a water surface while HD is capable to produce such film only on ionic subphase.

Atomic force microscopy (AFM) data testify to the high uniformity of the 2,4-heneicosandione film, as well as for the metal-containing derivatives. Properties of the films (1) and (3) on a solid substrate are also various.

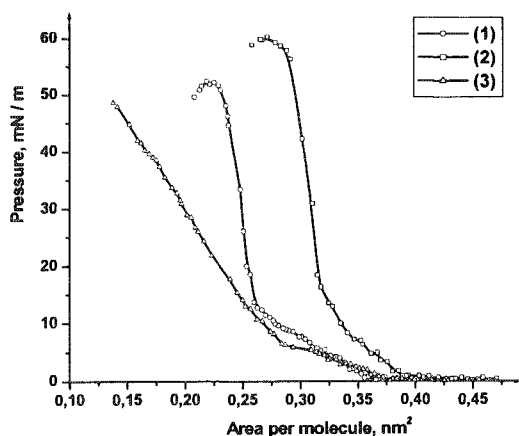


Figure 2. π -A isotherms for HD (1) and its copper complex $(\text{HD})_2\text{Cu}$ (2) recorded on aqueous interface and for HD on ionic subphase (3).

There was found by AFM extremely smooth surface film, the behenic acid, HD and $(\text{HD})_2\text{Cu}$ monolayers transferred by HP method on hydrophilic silicon surface and a little bit disordered for HD and amorphous for behenic acid and $(\text{HD})_2\text{Cu}$ (with numerous porous defects) on $\text{Si}/\text{SiO}_2/\text{OTS}$ surface. On the contrary, the best quality of multilayer film was observed in the case of $(\text{HD})_2\text{Cu}$ film transferred on hydrophobic silicon plate by vertical method.

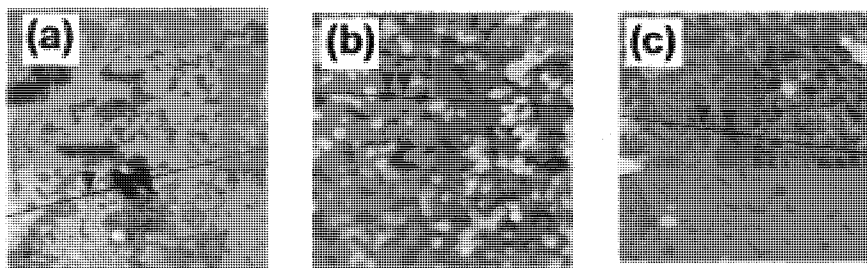


Figure 3. (a) AFM image of $(\text{HD})_2\text{Cu}$ monolayer film after artificial holes formation by AFM tip; (b) AFM image of HD monolayer film morphology after 5 min keeping it in water; (c) AFM image of $(\text{HD})_2\text{Cu}$ monolayer film morphology after 5 min keeping in water.

Adhesion of monolayer films to the silicon surface was estimated via force that should be applied during scanning to remove the material of monolayer from the surface. It was found a strong resistance of HD monolayer to AFM tip influence. It was impossible to make a hole into HD monolayer on hydrophobic surface by the standard oxide-sharpened Si_3N_4 AFM tips. Monolayer films of HD also showed high stability on hydrophilic surface, though the holes were formed at ~ 10 nN of the normal load. That suggests a strong interaction of polar heads of molecules with the silicon surface. $(\text{HD})_2\text{Cu}$ films were less stable on hydrophilic surface. In particular,

multilayer (HD)₂Cu film was essentially more labile and can be easily distributed on surface by AFM tip (Fig. 3a). In contrast, the monolayer film from HD molecules can be reorganized in presence of water on the silicon surface (Fig. 3b). (HD)₂Cu also changes the film morphology, but it remains in the monolayer form on solid surface (Fig. 3c). Thus, namely (HD)₂Cu monolayer can be used for subsequent silicon surface patterning by a microprinting technique.

Acknowledgements

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CLUSTER MECHANISMS OF NANOCRYSTAL FORMATION

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The cluster mechanisms of crystal nucleation and growth as well as crystal melting/dissolution are viewed. The nature of nanoparticles and the processes of nanostructured materials formation are discussed from the point of view of the cluster concept.

1 Introduction

The mechanisms of crystal phase formation are a key problem in materials science that has not clear comprehension still now. At present, the study of this problem is especially important in connection with the development of nanostructured materials. There are two different approaches to consideration of crystal nucleation/growth as well as crystal melting/dissolution processes [1,2]. In accordance with the first approach based on the atomic-molecular theory, the individual atoms or molecules take the leading part in these processes (the role of clusters is ignored). In accordance with the second approach based on the cluster theory, these processes are carried out mainly by means of clusters. Till recently the atomic-molecular theory was generally accepted. However, today many scientific data vote for the cluster theory. The aim of this paper is to analyze the main statements of the cluster conception of crystal phase formation and as a result to consider the nature of nanocrystal.

2 Crystal clusters

Clusters are formed by coalescing individual atoms (molecules) with each other, by coalescing individual atoms (molecules) with clusters formed before and by coalescing the clusters with each other [3]. In both last cases, the growth of clusters takes place. The reason of clusters formation is fluctuations of concentration (density) of medium occurring in the non-equilibrium state. It was shown that the rotation and spontaneous self-organization of the clusters take place during their coalescence [4]. Usually the clusters are unstable and dissociate into atoms (molecules). At the same time the atoms (molecules) associate into new clusters. Thus, there is a continuous association-dissociation process in the crystallizable medium. The stability of clusters is comparatively high when they have a great

number of bonds related to one atom [3]. The clusters can dissociate (melt/dissolve) completely or partially depending on their sizes as well as medium state. It is supposed that melting is characterized by the availability of both solid and liquid phases in clusters [3,5]. As a result, individual atoms (molecules) or groups of atoms (molecules) can separate from the cluster surface due to attenuation of the energy of bounds between the atoms (molecules) inside clusters. It is also supposed that melting of a cluster begins at the surface [6]. Thus, the outer liquid layer is formed. Then the melting front moves towards the cluster nucleus. Usually clusters contain up to several tens or hundreds of atoms (molecules) and have nanosize dimensions [1]. In particular, the clusters of different substances formed in solutions are of 1-10 nm in diameter [7].

3 Crystal nucleation, growth and melting/dissolution

3.1 Crystal primary nucleation

There are convincing evidences of pronounced arrangement of dissolved matter in the supersaturated solutions before the nucleation [1,2,7-9]. The reason of this arrangement is connected with the cluster formation. So, we may consider the supersaturated solution as a heterogeneous medium containing the clusters distributed in the solvent. The same conclusion is true for undercooled melts [1,9].

The clusters transform into the crystal nuclei having ability for the growth under certain conditions. Only clusters with some critical size $r_c = 2 \Omega \alpha / \Delta \mu$ can become potential centers of crystallization (here Ω is the specific volume of an atom or molecule involved into the cluster, α is the specific surface energy of interphase boundary and $\Delta \mu$ is the difference in chemical potentials for the phases) [10]. There are two main possible ways to transform the clusters into the critical crystal nuclei as a result of fluctuations [1]: (1) attachment of individual atoms (molecules) to the cluster and (2) coalescence of clusters with each other. It should be noted that in principle the critical nuclei formation as a result of coalescence of individual atoms (molecules) with each other is possible too. In all these cases the clusters must grow to the size $r \geq r_c$ in order to start a crystal growth process.

In accordance with the model of so-called "latent" phase clusters (LPC) [2] the energy of LPC formation from a vapor phase can be expressed as:

$$\Delta G = 4\pi r^2 \sigma + (4/3) \pi r^3 \Delta G_v + W, \quad (1)$$

where r , S and V are LPC radius, surface and volume, respectively, σ is the specific surface energy, ΔG_v is the specific volume energy, W is the surface electrical charge.

$$\Delta G_v = (RT/V_m) \ln(P/P_0), \quad (2)$$

where R is the universal gas constant, T is the temperature (K), P is the vapor pressure near the LPC with the radius r , P_0 is the equilibrium vapor pressure upon flat surface.

$$W = (Ze)^2/4\pi\epsilon\epsilon_0r, \quad (3)$$

where Ze is the charge of LPC, ϵ is the material permittivity, ϵ_0 is the permittivity of vacuum.

$$\sigma(r) = \sigma_0[1 - (2\delta/r)], \quad (4)$$

where σ_0 is the surface energy of a flat interface, δ is the "phase-boundary thickness" estimated to be 0.3 nm [2]. So, the energy balance can be finally expressed as:

$$\ln(P/P_0) = (2V_m\sigma_0/RT)[1 - (2\delta/r)] - [V_m(Ze)^2/16\pi^2\epsilon\epsilon_0r^4RT]. \quad (5)$$

For the nucleation from a solution the left side of the equation should be substituted by $\ln(c/c_0)$ where c and c_0 are corresponding concentrations. At the maximum of $\ln(c/c_0)=f(r)$ (at the maximum of supersaturation) the LPC are potential centers of crystallization and "latent" phase-to-crystal phase transition takes place.

Thus, there is no strong difference between clusters and critical crystal nuclei. Both clusters and critical nuclei are similar in their sizes and structure as well as their ways of formation. However, the critical nuclei are stable and can grow while the clusters are unstable at the given non-equilibrium state of medium. In the case of solutions, the probability of cluster-to-critical nucleus transformation is increased with a rise of supersaturation [1].

3.2 Crystal growth and crystal secondary nucleation

Generally, crystals grow by deposition of both atoms (molecules) and clusters on to the crystal surface. In solutions, the cluster mechanism dominates at the higher supersaturation. A semi-arranged layer of solution is formed near the crystal surface. The layer has the higher density and consists of the clusters that go to the crystal from the solution volume and concentrate at the crystal surface before deposition. The layer thickness is about 100 nm [8]. As a consequence, it can contain some tens of cluster monolayers. There are specific far-acting forces of a crystal lattice [11]. The range of their action is about 100-200 nm. Due to these forces the clusters involved into the semi-arranged layer are attracted to the crystal surface and simultaneously oriented relative to each other and to the crystal. As a result, the clusters arrange into the advantageous energy positions before the attachment to the growing crystal [1,8,12].

The crystal growth often is accompanied with the secondary nucleation. One of the reasons of secondary nuclei appearance is related to the clusters removed from the semi-arranged layer. In particular, size separation of crystals grown in solutions by centrifugation revealed clusters with the sizes of 5-10 nm [8]. It was shown experimentally that these clusters were separated from the semi-arranged layers under the action of centrifugal forces. An existence of clusters in the semi-arranged layer is also confirmed by the experiments on growth of vibrating crystals in solutions. The experiments show that vibrations cause an increase of the growth rate and the improvement of crystal structure [8]. It is explained by the action of vibrations on the clusters located to the semi-arranged layer.

3.3 *Crystal melting/dissolution*

Taking into account the features of the cluster melting mentioned above it is possible to consider the process of crystal melting as follows [3]. In the course of initial heating the cluster melting is initiated and, as a consequence, the mobility of clusters is increased. As a result, the crystal nearby the melting point consists of separated clusters surrounded with the unstructured layers of atoms (molecules). Thus, there is a specific transition period when the solid-state structure transforms into the liquid-state one. At the next stage of the process the clusters as well as the individual atoms (molecules) separate from the crystal surface. Then separated clusters dissociate into individual atoms (molecules). The transition period corresponds to so-called pre-melting state of the crystal when a lot of mobile clusters are formed inside it [13]. Also there is an opinion that melting occurs when the superheated crystal spontaneously generates a sufficiently large number of spatially corrected destabilized particles and that the accumulation and coalescence of these internal local lattice instabilities constitute the primary mechanism for homogeneous melt nucleation inside the crystal, in lieu of surface nucleation for equilibrium melting [14]. Analogically, it is possible to consider the process of crystal dissolution [8].

4 **Crystal nanoparticles**

Taking into account the considered cluster concept we may conclude that crystal nanoparticles as objects of nanotechnological applications are stable particles of matter having the size $r \geq r_c$. Indeed, the particles with the size $r < r_c$ are unstable clusters and the changes of their structure depend on the number of atoms (molecules) involved into them [15]. The experiments show that the structure of nanoparticles is heterogeneous. They consist of a number of specific fragments [16]. Thus, one may consider the fragments as the clusters incorporated into the nanoparticles in the course of their formation.

Properties of the crystal particles depend on their size. In particular, when the particles are reduced in size to less than 5-10 nm, a significant reduction of the melting point takes place [17]. This phenomenon can be connected with the mechanism of melting mentioned above. Besides, it can be explained by considering the surface energy contribution to the Gibbs free energy of nanoparticles. When the particles are reduced in size, a significant fraction of atoms is located on the surface, and the surface energy has a significant effect on the melting point. So, it has been postulated that melting begins with the formation of a liquid "skin" layer around the particle.

There are two approaches to fabrication of nanostructured materials based on liquid-to-crystal or crystal-to-liquid transitions. The first approach is crystallization of a melt. This way is not widely spread now. Meantime, it is rather promising. Recently it was shown that it is possible to form bulk nanostructured alloys with grains of 3-6 nm by rapid solidifying of the melt [18]. This effect is connected with the formation of a lot of clusters in the undercooled melt and their transformation into the critical nuclei.

The second approach is nanopowder sintering. The nanoparticles are susceptible to sintering due to greatly reduced melting point. During heating of a nanopowder the pre-melting process mentioned above is initiated. Liquid layers are formed at the surface of the particles. Besides, liquid inclusions are formed inside them and the particles go to so-called semi-solid state. As a result, contacts between the particles are formed mainly by liquid phase mechanism. If liquid fraction is rather high, the initially small particles coalesce into the large aggregates. Therefore it is very important to adjust the energy and time parameters of the process in order to get the structure with required grains.

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MULTIMODE SPM METHODS FOR NANOMETER RESOLUTION STUDY OF LANGMUIR-BLODGETT FILMS

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Surface morphology of the dithienylpyrrole LB films has been investigated by multimode SPM as a function of their deposition parameters, and the type of the substrate used. It was found that the morphology influences the size and shape of the nanostructures resolved as well as the reliability of the process.

1 Introduction

Langmuir-Blodgett (LB) films have many applications in the areas of molecular electronics, non-linear optics, cell membranes, and biosensors [1,2]. Most of the potential applications of LB films are based on the premise of perfect molecular layering and orientation. Scanning probe microscopy (SPM) provides new possibilities for imaging thin organic LB films as well as for their controlled and reproducible nanomodification. The size and shape of the nanostructures are strongly dependent on the LB film surface morphology. Hence, studies of the ordering in these molecularly layered films are of critical importance. In this paper the surface morphology of dithienylpyrrole LB films investigated by multimode SPM is presented and discussed.

2 Experimental procedures

The $\alpha\alpha'$ - β -hexadecyldithienylpyrrole films (Y-type) were prepared by usual LB technique onto freshly cleaved HOPG and mica at a deposition speed of 6.7 mm/min and surface pressure of 35 mN/m, if FeCl_3 subphase was used, and at a deposition speed of 17 mm/min and surface pressure of 35 mN/m, if $\text{Fe}(\text{NO}_3)_3$ subphase was used. The investigation of the films and their nanomodification were performed with SPM Solver-P47 (NT-MDT, Moscow).

3 Results and discussion

Three distinct morphology features were observed on three monolayer LB films deposited on mica from $\text{Fe}(\text{NO}_3)_3$ subphase: the first is islands with curved boundaries, similar to fractals; the second is numerous large grains; the third is tore-like clusters from grains. The LB films deposited on mica from $\text{Fe}(\text{NO}_3)_3$ subphase demonstrate no essential changes in morphology as the number of monolayers increases. The LB films deposited on mica from $\text{Fe}(\text{NO}_3)_3$ subphase were free of hole defects and seemed, in particular, well suited for nanoscale lithography. By increasing the force to 70 nN when scanning with AFM, it was possible to scratch square holes of nanoscale size in such LB films (Fig. 1).

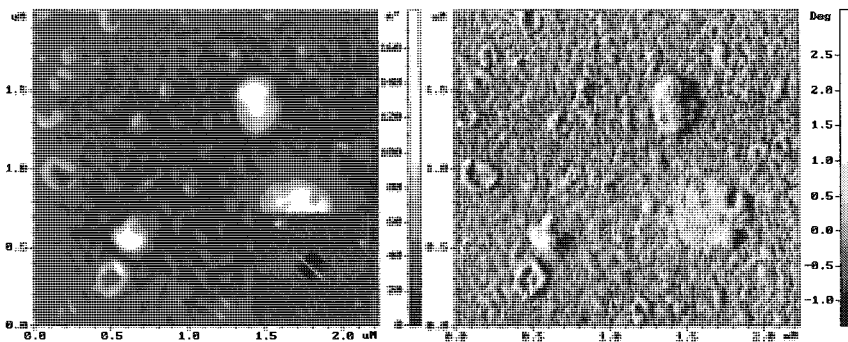


Figure 1. AFM images (height and phase) of the dithienylpyrrole LB film on mica (3-monolayers, $\text{Fe}(\text{NO}_3)_3$ subphase). The inset is AFM image (height, contact mode) of dithienylpyrrole LB film on mica (3-monolayers, $\text{Fe}(\text{NO}_3)_3$ subphase) with a written square hole.

It was found that morphology of three monolayers LB films deposited on mica from FeCl_3 subphase changes drastically. The film is islandlike without any tore clusters and possesses a small number of large grains. With increasing number of monolayers the morphology of LB films varies dramatically. The surface of the seven monolayer LB film on the mica from FeCl_3 subphase has grains ranging from 20 to 50 nm. Large grains of the order of from 20 to 200 nm were observed on the film surface regardless of the number of layers and subphase. These, apparently, can be either FeCl_3 ($\text{Fe}(\text{NO}_3)_3$) crystals, originated from the adhesion of the subphase drops on the film surface or clusters, splitted out from the film during the process of its formation at the meniscus from the Langmuir layer on the subphase surface. From a rather homogeneous phase image and the adhesion force map with no contrast we could conclude that the observed grains are clusters of the amphiphilic molecules of dithienylpyrrole. The modification of the LB films deposited on mica from FeCl_3 subphase was performed by increasing the force when scanning with AFM in semicontact mode of operation. The written figures “1” and “2” (with size of ~8 nm in height and ~150 nm in width) appeared

as convex up have been formed by grains of the amphiphilic molecules of dithionylpyrrole (Fig. 2).

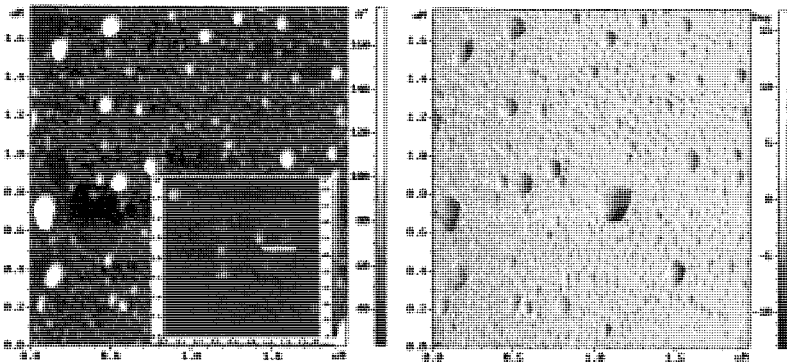


Figure 2. AFM images (height and phase) of the dithionylpyrrole LB film on mica (7-monolayers, FeCl₃ subphase). The inset is AFM image (height, semicontact mode) of dithionylpyrrole LB film on mica (7-monolayers, FeCl₃ subphase) with written figures “1” and “2”.

The grain structure of the two monolayer LB film deposited on HOPG from Fe(NO₃)₃ subphase was distinct with the grain size from tens to hundreds of nanometers. Unlike the films formed from Fe(NO₃)₃ subphase, ones deposited from the FeCl₃ subphase consist of randomly connected islands with curved boundaries (Fig. 3). With increasing number of monolayers the morphology of LB films deposited on graphite from FeCl₃ subphase does not practically change. The AFM modification of six monolayer LB films deposited on graphite from FeCl₃ subphase was performed by applying the voltage (5V, 10V) between the tip and the substrate in the contact mode [3].

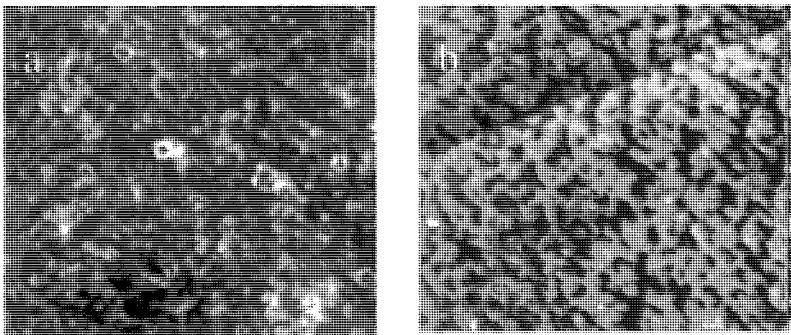


Figure 3. (a) - AFM image (height) of the dithionylpyrrole LB film on HOPG (2-monolayers, Fe(NO₃)₃ subphase); (b) - AFM image (height) of the dithionylpyrrole LB film on HOPG (2-monolayers, FeCl₃ subphase).

In conclusion, the investigations carried out on the LB films by SPM methods have demonstrated high mobility of the LB films with a tendency for restructuring mainly in the process of formation. The LB film surface morphology changes drastically with varying number of monolayers, subphase and the type of substrate used.

Acknowledgements

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STRUCTURE AND NANOHardNESS OF PVD COMPOSITE NANOSIZED Ti-Zr-N FILMS

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Condensation combined with ion bombardment allows to fabricate nanostructured quasibinary (TiN/ZrN) and triple (Ti-Zr-N) nitride coatings. These coatings can be ranked as a superhard material due to their mechanical properties.

1 Introduction

Thin hard coatings of nitrides of transitional metals fabricated by physical vapour deposition (PVD) are now widely used as corrosion and wear resistant protective coatings. They possess improved mechanical properties, such as a high oxidation and corrosion resistance, wear resistance and hardness. A multilayer thin films made by controlled alternating deposition of two materials allows to create nanostructured materials possessing some important characteristics. Superhigh hardness (50 GPa) and high elasticity have been reported by several research groups for TiN-containing systems such as TiN/NbN, TiN/VN, TiN/TaN and TiN/ZrN [1-3]. Such multilayered structures belong to the class of superhard materials. The ternary nitride systems of Group IV-VI transition metals forming continuous solid solutions ($\text{MeI}_x\text{MeII}_{1-x}\text{N}$) with NaCl-type face-centered cubic structure should be also related to this class.

TiN/ZrN and (Ti,Zr)N coatings were produced by vacuum-arc deposition with simultaneous and alternating cathode-ion bombardment of plasma flux of Ti and Zr in N_2 gas atmosphere. Carbon steel st3 was used as a substrate material. Substrates were cleaned by Ti^+ ion bombardment during 1 min with the substrate bias being -1 kV, arc current of Ti cathode 100 A, and vacuum in the chamber 10^{-5} Pa. All films deposition was initiated by introducing N_2 gas at a pressure of 10^{-1} Pa into the vacuum chamber, and 10 nm (Ti,Zr)N films were obtained by simultaneous deposition of Ti and Zr ions. Multicomponent coatings were deposited using different substrate bias up to -210 V. Multilayer thin films were obtained by alternating deposition of TiN and ZrN using a substrate bias -120 V. To produce coatings of different microstructure the thickness of one layer varied from 10 to 50 nm. The preferred orientation and residual stresses in (Ti,Zr)N and TiN/ZrN films were investigated by X-ray diffraction (XRD) using CuK_α radiation. The

microstructure of the coatings and their thickness were studied by Scanning Electron Microscopy (SEM). The nanoindentation responses of (Ti,Zr)N and TiN/ZrN films were determined using a Nano Indenter-II instrument with the triangular Berkovich diamond indenter tip. The measurements procedure was as follows: load to maximum, unload to 10% of maximum load, hold for 50 s, load to maximum, hold for 200 s, and completely unload. The maximum load was 60 mN and minimum of 10 indent sequences was used. Sample hardness and modulus of elasticity were calculated from the first 30% of the second unloading segment using the technique developed by Pharr and Oliver [4].

2 Multilayer thin films

XRD investigations show that TiN/ZrN films consist of TiN and ZrN layers with cubic structure and (111)-preferred orientation. Appearance of (111)-preferred orientation is connected with the influence of incident ions and heating. For modulation period (the thickness of one lamella of TiN together with one lamella of ZrN) $\Lambda=20$ nm the superstructure peak due to a long range in the coating, was found. Also, the superlattice peaks of multilayer films TiN/MoN for modulation period 9 nm, TiN/NbN – 12 nm and TiN/TaN – 11 nm [5] appear. The mechanism of superlattice formation is explained by blocking interlaminar layers and dislocation in layer interfaces and within layers. This, in turn, is a result of differences in the shear modulus of the constituents, strain for small periodicity multilayers with a significant lattice mismatch, grain boundaries and defects within the layers. The superlattice peak positions of the high-angle diffraction spectra are dependent solely on the average lattice spacing of the constituent layers, modulation periodicity and can be described by the kinematic step model [6]. Fig. 1 illustrates lattice deformation of TiN and ZrN as a function of the modulation period Λ .

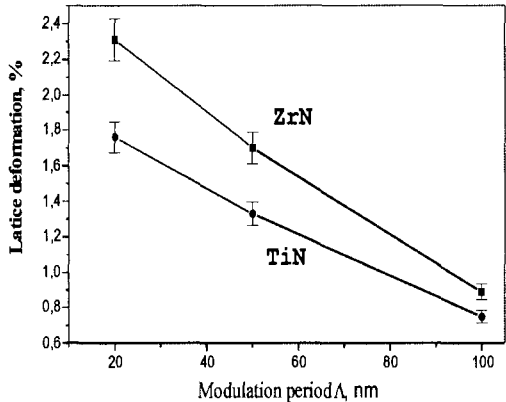


Figure 1. Lattice deformation of TiN and ZrN as a function of the modulation period Λ .

Residual stresses were measured by using (111) reflection. The results are presented in Table 1 together with sizes of coherent scattering areas. The residual stresses obtained are of a compressing type. Their absolute value increases with decreasing Λ attaining 15 GPa.

Table 1. XRD analysis results.

Modulation period (Λ), nm	Residual stress, GPa	Size of blocks, nm
20	-15.1	8.4
50	-10.8	19.7
100	-7.3	26.1

The microstructure of (Ti,Zr)N and TiN/ZrN films have some features connected with a columnar growth of coatings. The size of the crystallites (~100 and 55 nm for (Ti,Zr)N and TiN/ZrN, correspondingly) rises as the distance from the substrate-coating interface increases.

For TiN/ZrN multilayers (Fig. 2) nanohardness increases and modulus of elasticity decreases with decreasing modulation period Λ . However, in literature the decreasing of Λ to 5-10 nm leads to further increasing of hardness (for example for Λ =7.5 nm hardness of TiN/CrN films achieves 40 GPa).

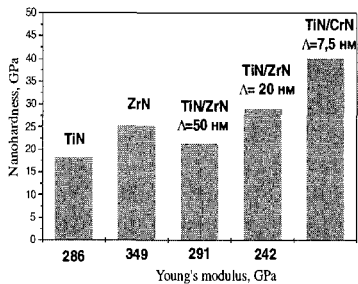


Figure 2. Nanohardness of multilayer films.

3 The ternary nitride system

According to XRD study mononitrides TiN and ZrN are completely mutually soluble in the Ti-Zr-N system. The diffraction maxima of the ternary coatings lie between those of appropriate binary nitrides, and thus the lattice parameter of (Ti,Zr)N is between that of TiN and ZrN. A (Ti,Zr)N solid solution was formed under the whole range of substrate bias in which the multicomponent Ti-Zr-N films were deposited. The high intensity of the (Ti,Zr)N (111) peak, as compared with the theoretical values, indicates that (Ti,Zr)N grains grow in the {111} orientation. The lattice parameter was calculated from the peak position to be 0.404 nm for the coatings independently from the bias voltage. The coatings thickness was from 6.6 to 7.5 μ m.

The (Ti,Zr)N grains are columnar, aligned normal to the substrate, with an average diameter of 100 nm. The elemental composition of the coatings is shown in Table 2. The compositions of the coatings deposited at different substrate bias were found to be identical. Concentrations of Ti and Zr do not depend on the substrate bias.

Table 2. Elemental composition of the Ti-Zr-N coatings.

Bias voltage, V	Ti(at.%)	Zr(at.%)	N(at.%)	C(at.%)
0	21±2	18±2	44±8	17±3
210	23±2	17±2	43±7	17±3

The nanohardness of the (Ti,Zr)N coatings as a function of the applied bias is shown in Fig. 2. The coatings show significantly higher nanohardness compared with that for binary coatings deposited under identical conditions.

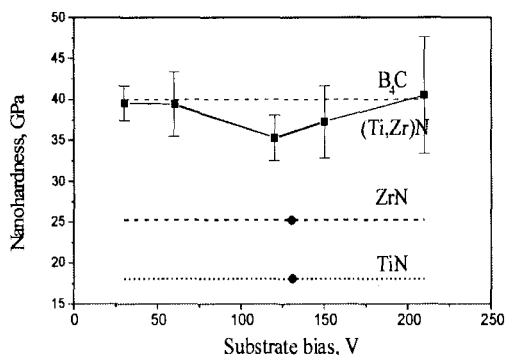


Figure 3. Nanohardness of the multicomponent (Ti,Zr)N coatings.

Nanoindentation tests of the samples show that hardness of (Ti,Zr)N films (Fig. 3) increases in comparison with TiN and ZrN films approaching to the hardness of boron carbide B₄C (40 GPa). The effect of increased hardness is probably due to a solid-solution strengthening mechanism.

In conclusion, PVD technology with simultaneous and alternating cathode-ion bombardment of plasma stream of Ti and Zr in N₂ atmosphere allows to fabricate new class of superhard materials.

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SYNTHETIC APPROACH FOR PREPARATION OF NANOMETER-SIZED NON-LINEAR OPTICAL ADVANCED MATERIALS

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The nanoparticles of non-linear optical material KTiOPO_4 (KTP) were synthesised through metal-organic precursors, prepared by reaction of alkoxides $(\text{RO})_3\text{P}(\text{O})$, $\text{Ti}(\text{OR})_4$, and KOR (R=Et, Pr, Bu) in alcohol solution. The precursor thermal decomposition (650–900°C) resulted in a single-phase KTP of different, preferably spherical, morphology. The dimension of produced particles is ranged from 45-50 up to 800-1500 nm.

1 Introduction

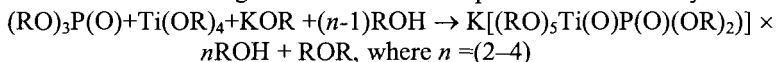
Miniaturising tendency led to new ways of application for known industrial materials: LiNbO_3 , KTiOPO_4 , BaTiO_3 using nano-dimensional effect. Controlling of nanocrystals shape and size is a hot research subject. Potassium titanyl phosphate KTiOPO_4 (KTP) has been used as second harmonic generation (SHG) crystals and as waveguides in optical devices. The drawback of KTP grown by hydrothermal or flux methods is inclusion of impurities. In contrast, the sol-gel method allows obtaining of high-purity materials at lower temperatures. Recently, KTP thin films [1] and fibres [2] have been synthesised from metallo-organics.

We studied the possibility of crystalline KTP nanoparticles formation and determined the influence of carbon chain length in metal-organic precursors on the shape and dimensions of nanoparticles.

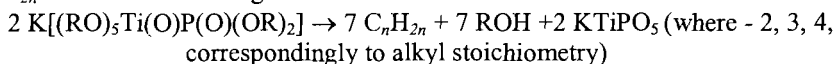
2 Experimental

Preparation procedure. Tri-*n*-alkyl phosphate $((\text{RO})_3\text{P}(\text{O}))$, titanium tetra-alkyloxide $(\text{Ti}(\text{OR})_4)$ and potassium alkyloxide (KOR) (R is *n*-alkyl: Et, Pr, Bu) (all Aldrich GmbH) were used as starting reagents. The ROH alcohols were dried over magnesium alkyloxide and distilled before use. All synthesis stages were conducted in dry argon atmosphere. An equimolar mixture of $(\text{RO})_2\text{P}(\text{O})(\text{OH})$ and $\text{Ti}(\text{OR})_4$

was dissolved in absolute ROH alcohol and refluxed during 17 h. After addition of KOR stoichiometric amount the solution was refluxed for 20 h. This treatment resulted in formation of homogeneous and colorless precursor solution by reaction:



The unctuous concentrated solution of precursor was obtained by solvent dilution. The precursor thermolysis was performed at 100–850°C in specially constructed chamber equipped with beam-heater and mass-spectrometric (MI-101) control of the gas composition. The decomposition is accompanied by elimination of C_nH_{2n} molecules according to the scheme:



Analysis and spectroscopic study. The elemental analysis was performed with an ICP-6000 spectrometer. The precursors crystallization was studied by thermal analysis methods (TG85). The samples were analysed by IR spectroscopy (Nicollet, FTIR-7500) and powder X-ray diffraction (PXRD, DRON-3). The morphology of surface was studied by scanning electron microscopy (SEM) (JEOL, JSM-6100). The density of KTP particles was determined by a sink-float method. Local x-ray analysis was performed using Link ISIS microanalysis system (Si:Li detector) mounted on Jeol 2000 FX microscope. Bruker-400 apparatus was used for ^{31}P , ^{13}C and ^1H NMR study of precursor solution. The YAG:Nd $^{3+}$ SHG was measured on LS-10 device.

3 Results and discussion

The FTIR spectra of initial solutions and resulted complex precursors $\text{K}[(\text{RO})_5\text{Ti}(\text{O})\text{P}(\text{O})(\text{OR})_2]$ confirmed rearrangement of bonds with the bridge Ti–O–P formation (Fig. 1). The ^{31}P NMR spectra of precursors are identical and typical for organometallics containing P=O and P–O–R bonds ($\delta^{31}\text{P}$ -0.089(2), -0.141(4), -0.186(4), -0.230(3), -0.274(2), -0.319(1), -0.378(7) ppm), where $\delta^{31}\text{P}$ phosphorus chemical shift (ref. to H_3PO_4).

The process of precursor thermal transformation has been studied in the temperature range of 100–850°C.

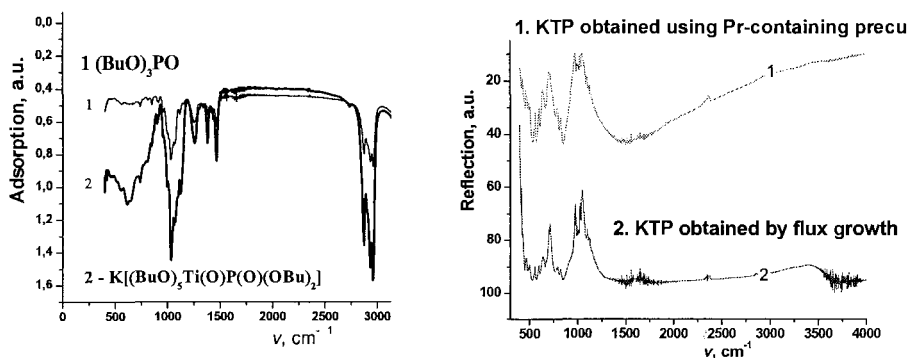


Figure 1. FTIR spectra of KTP-precursor solution and initial butylphosphoxide (left panel); DRIFT spectra of single-phase KTP obtained by thermolysis (right panel).

Earlier [2], for preparation of KTP from $\text{Bu}_2\text{Et}_4\text{O}_8\text{TiPK}$ a two-staged process was proposed: calcination at 400°C and KTP crystallization at 650°C , although, as determined by thermal analysis [2], the KTP crystallization occurs at higher temperature (690°C). Thus, this experimental condition for KTP-preparation does not give a satisfactory result and could not be applied for nanotechnology.

As it is known, the organic-inorganic complexes combust at high temperatures. We proposed to use this high rate chemical reaction for manufacturing of nano-sized particles with a controlled dimension. The temperature of ligand thermal destruction insignificantly changes with R increasing in studied composition interval. Eliminating of C_nH_{2n} and ROH occurs in two stages and is completed at about 250°C . The exact reaction mechanism including possibility of precursors polymerization needs further study.

The several thermolysis regimes were explored, the low (250°C) and intermediate (655°C) ones led to formation of amorphous solid with stoichiometry close to that for $\text{K}_2\text{Ti}_2\text{O}(\text{HPO}_4)_2$ and admixture of rutile- TiO_2 . The optimal thermal regime of the process was found to be in the temperature interval $700\text{--}850^\circ\text{C}$ which is below the ferroelectrical phase transition. Such conditions enables generation of extremely small particles.

The analysis data and PXRD parameters of developed particles are identical to those of KTP. The DRIFT-spectrum of KTP powder obtained from propyl precursor and by flux growth are represented (Fig. 1). High reaction rate is one of the necessary conditions for nanocrystalline particles producing due to atomistic level of interaction at self-assembly into complex oxide material. The length of carbon chains in precursors and energetic of burning of corresponding *n*-ethylenes determines the particles dimensions, while spherical shape is uniform for all precursors composition and radical substituents. The latter fact confirms a general similarity in KTP particle formation. The speedy gas elimination and combustion result in formation of dense spherical particles. The density ρ of such particles are practically identical ($\rho_{\text{float}} = 2.97 \text{ g/cm}^3$, 98% theor.) to KTP crystals grown from

flux melts. The particles of KTP can be of different size due to an influence of the complex composition. In Fig. 2 nanosized particles obtained by Bu-containing precursor thermolysis and by direct heating in air are represented.

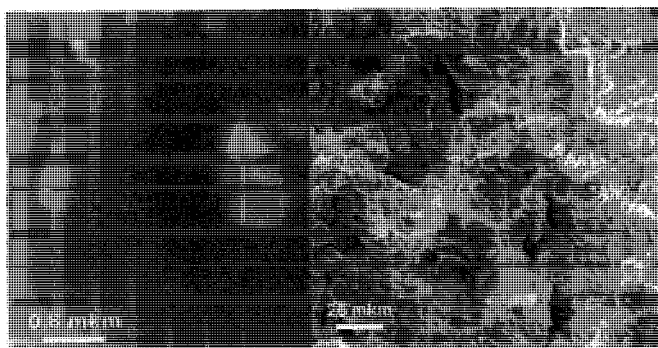


Figure 2. SEM image of KTP nanoparticles obtained by thermolysis (left panel) and direct heating in air (right panel).

The use of precursors with R of low link carbon chains results in producing of particles of average size ranged from 45-50 nm for R-methyl, 210-250 nm for R-Propyl, to 800-1500 nm (R-Butyl) at otherwise identical processing conditions: temperature, pressure, heating rate.

The SHG effect, which is on 25% greater than for reference (KTP-crystals) was observed. This data confirm significant contribution of nano-effects in the property improvement.

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GERMANIUM QUANTUM DOTS IN SiO₂: FABRICATION AND CHARACTERIZATION

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A new method of forming Ge nanocrystals in SiO₂ based on molecular-beam epitaxy combined with rapid-thermal processing is presented. We demonstrate that the method allows the formation of a high aerial density ($\sim 5 \times 10^{11}$ dots/cm²) of small spherical dots (~ 4 nm in diameter) of a narrow size distribution located at a controlled and well-defined distance from the Si/SiO₂ interface, and that these dots show a significant memory effect.

1 Introduction

Presently a huge interest is generated by both basic-physics and applied aspects in the production of semiconducting nanoparticles embedded in a silicon dioxide (SiO₂) layer on top of a Si substrate [1,2]. The understanding of the fundamental properties of such a material as a result of the spatial confinement in three dimensions is a very challenging task and of course, the prerequisite for a successful exploitation of these new materials containing nanoparticles. Two major areas of application are at the moment the prime movers of this field: making of an efficient Si-light source with the help of nanocrystals (ncs) [3], and the use of nanocrystals as charge storage elements in memory devices [1]. In this paper we in particular focus on the latter subject, in which nanoparticles are embedded into the silicon dioxide (SiO₂) layer of a metal-insulator-semiconductor (MOS) device. The perspectives are making of high speed and low power consuming logic and memory devices [1].

The use of a so-called floating gate, composed of isolated nanodots in the gate oxide of a field effect transistor and located in close proximity to the transistor channel, reduces the problems of charge loss encountered in conventional FLASH memories, allowing for thinner injection oxides and hence, smaller operating voltages, better endurance, and faster write/erase speeds [1]. The performance and the success of such a memory structure strongly depend on: (a) the process ability for making uniform and reproducible thin tunnel oxides and (b) the characteristics of the islands (such as crystallinity, size, shape, orientation, spatial distribution) that influence both the potential energy of trapped electrons and the Coulomb blockade energy, which prevent the injection and storage of more electrons [1].

Self-assembling of silicon or germanium nanocrystals in SiO_2 layers has been studied by a large number of groups and strong memory effects in MOS devices using such oxides were reported [4-6]. To our knowledge it has not yet been demonstrated whether Si or Ge is the better choice as the nanocrystal materials in such memory devices. It is, nevertheless, clear that differences in electronic structure, melting temperatures, diffusivity, solubility etc. between Si and Ge influence the memory characteristics and the dot-formation kinetics. There are experimental indications for ion-beam synthesized nanocrystals that, in that particular case, nanocrystals of Si are to be preferred [7]. A thorough experimental comparison of Si and Ge nanocrystals as charge storage elements in memory devices is, however, still lacking.

A variety of different methods has been suggested for the fabrication of Si and Ge nanocrystals in SiO_2 since Tiwari et al. [4] in 1996 proposed and demonstrated a Si-nanocrystal memory device produced by chemical-vapor deposited layers of Si and SiO_2 , e.g. radio frequency cosputtering techniques [5], different variants of chemical vapor deposition (CVD) [1], and aerosol synthesis [8]. Ion implantation of Si or Ge into SiO_2 followed by appropriate heat treatment appears promising since well-defined depth and size distributions of the Si or Ge nanocrystals can be achieved by adjusting the ion implantation annealing conditions [6].

In the present work we will discuss a new growth technique of Ge nanocrystals in SiO_2 which we have developed recently, based on molecular-beam epitaxy (MBE) combined with rapid-thermal processing (RTP). The grown structures have undergone very detailed structural characterizations and are at the moment in the process of being electrically characterized.

2 The method

The fabrication method, which we have developed, is based on three steps (see Ref. 9 for a more detailed description). The two first steps are illustrated in Fig. 1 and the third step in Fig. 2. A Ge layer of a few monolayer thickness is first deposited by MBE on a thin SiO_2 layer (~5 nm) thermally grown on a p-type, (001) Si wafer, followed by the deposition of a Si capping layer of a thickness of about 4 nm (Fig. 1a). The motive for depositing the Ge layer on a pre-grown SiO_2 is to

prevent Ge segregation to the Si/SiO₂ interface during the subsequent oxidation process and to fix the thickness of the oxide layer (called the tunnel oxide) between the Si substrate and the Ge nanocrystals. The oxidation of the Si-cap and Ge layer is done by RTP at a temperature of 800°C. When the oxidation has just reached the

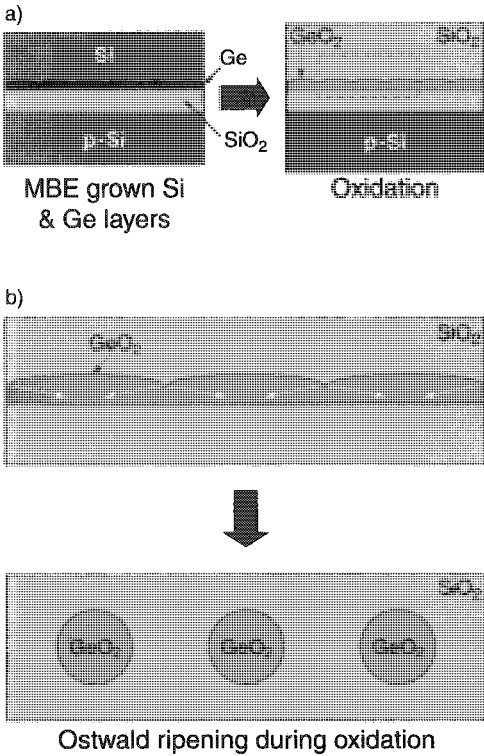


Figure 1. Sketch of the MBE-growth and oxidation processes: b) is an expansion of the dotted-line enclosed area of a) illustrating the oxidation process.

transforms these connected islands into GeO₂ dots (Fig. 1b). The oxidation time is typically 14 min. The self-assembling phenomenon of the Ge-nanodots in SiO₂ can be explained by the Ostwald ripening mechanism [10], which describes the growth of larger particles at the expense of smaller particles. Shklyaev et al. [11] has shown that MBE-grown Ge layers form a high-density of hemispherical, connected Ge-islands on a Si substrate covered with a thin SiO₂ layer (illustrated in Fig. 1a). This structure forms the starting point of the Ostwald ripening mechanism (as illustrated in Fig. 1b). It requires diffusion of Ge atoms from the peripheral/valley regions of the Ge-islands towards their respective centers to construct spherical dots for achieving greater volume to surface ratio, which is preferable to get a lower energy state. All the

pregrown SiO₂ layer the Ge layer has transformed into connected GeO₂ islands as revealed by transmission electron microscopy (TEM). A short prolongation of the oxidation process

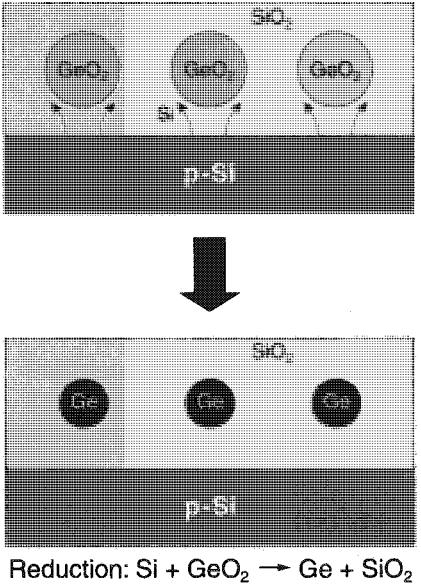


Figure 2. Sketch of the reduction process.

islands are found by TEM to be connected until complete oxidation of the Si capping layer. Thus, most of the Ge-dot formation takes place after complete oxidation of the Si capping layer but still during the oxidation process.

The Ge layer is oxidized during the dot formation. For this reason a reduction process is essential to recover the Ge-nanodots from their oxide state. During thermal treatment in N_2 at elevated temperature, the GeO_2 clusters are reduced by Si-atoms arriving from the SiO_2/Si interface according to the chemical reaction $Si + GeO_2 \rightarrow Ge + SiO_2$ [12]. The reaction proceeds spontaneously and rapidly when the mobile Si atoms come in contact with the reaction interface of GeO_2 , and interdiffusion of Si and Ge takes place because of very large driving force originating from a large difference in Gibbs energies of formation for pure GeO_2 and SiO_2 [12]. It is expected that some dot growth take place during the reduction process according to the Ostwald ripening mechanism. We have, however, not yet any experimental evidence for that.

3 Transmission-electron microscopy investigations

The whole fabrication process has been optimized with respect to negligible Ge segregation at the Si/SiO_2 interface, a uniform dot-size distribution around 4 nm, a tunnel-oxide thickness of about 4 nm, a dot density $\leq 10^{12} \text{ cm}^{-2}$ (electron transport between the dots was observed for a dot density larger than 10^{12} cm^{-2} in agreement with theoretical expectations [13]) and the largest possible charge storage capability. The optimal processing conditions (also called the optimized conditions in the following) were found to be 14 min oxidation at 800°C in O_2 followed by 30 s reduction at 950°C in N_2 , and a Ge-layer thickness $\leq 0.7 \text{ nm}$. In the following, examples will be given of samples produced under non-optimized as well as optimized conditions.

Figs. 3-5 show typical cross-section TEM (XTEM) micrographs of an as-grown sample (Fig. 3), after oxidation (Fig. 4), and after the reduction (Fig. 5). The micrographs are taken with the electron beam direction close to the (110)-zone axis in strongly underfocused condition. In this condition the Ge nanodots show a dark contrast on a grey background. The samples have been processed under the optimized conditions and the Ge layer was 0.7 nm thick. The hemispherical structure of the as-grown Ge layer can be recognized (Fig. 3), as also observed by Shklyaev et al. [11]. Note that

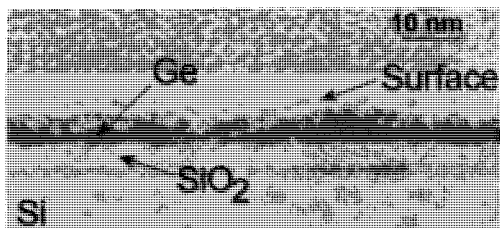


Figure 3. XTEM micrograph (bright field) of an as-grown sample containing 0.7 nm Ge layer.

the Si/SiO₂ interface is very flat. It appears from Fig. 4 that already prior to the reduction process some of the Ge dots show a strong contrast, which is indicative of partial transformation from GeO₂ to Ge (the contrast between GeO₂ and SiO₂ is weak).

Following the reduction process, spherical and well-separated Ge-ncs embedded in the SiO₂ layer are clearly observed (Fig. 5). The average distance of the dots from the Si substrate has been extracted from such XTEM micrographs. It depends on the thickness of the pre-grown SiO₂ layer and a typical value for a 5 nm thick pre-grown SiO₂ layer is 4.4 ± 1.4 nm.

The mean size and density of the dots are measured under the same imaging conditions but on plan view specimen. An example of such plan-view TEM micrographs of a sample processed under optimized conditions is shown in Fig. 6. The dot size is around an average value which for this particular case is found to be 4.5 ± 1.8 nm. A typical value of the aerial density is $5 \times 10^{11} \text{ cm}^{-2}$.

The crystalline nature of the Ge dots is evidenced in HREM images such as the one shown in Fig. 7. In large dots (~ 7 nm) twinning of the {111} planes is observed



Figure 4. XTEM micrograph (bright field) of a sample containing a 0.7 nm Ge layer, oxidized at 800°C for 14 min in O₂. The light black dots in the SiO₂ layer represent the partially reduced GeO₂ clusters.



Figure 5. XTEM micrograph (bright field) of a sample containing 0.7 nm Ge oxidized at 800°C for 14 min in O₂ followed by reduction at 950°C for 30 s in N₂.

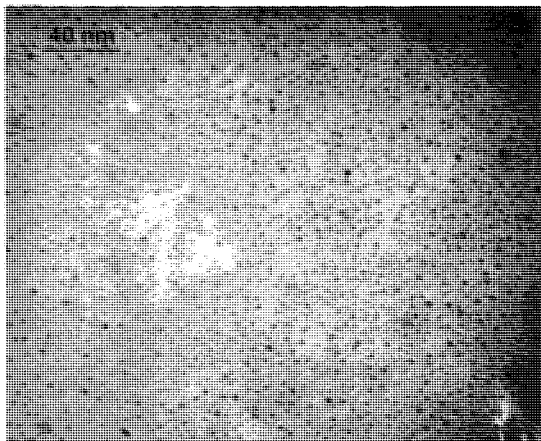


Figure 6. Plan-view TEM micrograph (bright field) of a sample containing a 0.7 nm Ge layer, oxidized at 800°C for 14 min in O₂ followed by reduction at 950°C for 30 s in N₂.

while the distance from the dot to the substrate could be as small as 2 nm.

The thickness of the deposited Ge layer is found to play a crucial role for the development of the Ge nanocrystals. The best results with respect to size uniformity and aerial dot density have been obtained with a Ge thickness of 0.7 nm. Fig. 8 shows a XTEM micrograph of a sample with a 0.9 nm Ge layer after the reduction process. An optimization procedure, similar to the one, which has been performed in the case of the 0.7 nm Ge layer thickness, has not yet been performed in the case of the 0.9 nm Ge layer. We have, however, not found process parameters which would result in a uniform size distribution. The example shown in Fig. 8 is typical. A Ge layer thickness smaller than ~ 0.7 nm results in a low aerial density ($\leq 5 \times 10^{11} \text{ cm}^{-2}$) but otherwise in a uniform size distribution (not shown). Thus, it can be concluded that the Ge-layer thickness of 0.7 nm results in close to optimal conditions. We speculate that an optimal hemispherical structure of the as-deposited Ge film is achieved for the Ge-layer thickness of 0.7 nm or below for the present deposition conditions. This is currently under investigation.

The advantage of using MBE for the deposition of the Ge and Si layers is the

precision by which very thin (e.g., 0.7 nm) uniform layers can be deposited.

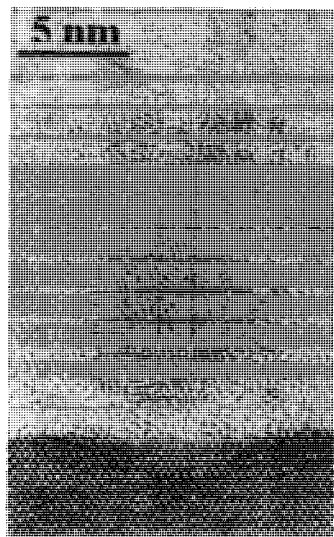


Figure 7. High-resolution TEM image of a crystalline isolated Ge-nanodot.



Figure 8. XTEM micrograph (bright field) of a sample containing a 0.9 nm Ge layer oxidized at 800°C for 14 min in O_2 followed by reduction at 950°C for 30 s in N_2 .

4 Capacitance-voltage characterizations

The memory behavior of the oxide layers with embedded Ge-nanodots was investigated through high-frequency capacitance-voltage (C-V) measurements of aluminum (Al) gate capacitors. A strong evidence of charge storage effect in the crystalline Ge-nanodot layer is demonstrated in Fig. 9 by the anticlockwise hysteresis behavior of the C-V curves of a MOS capacitor produced under

optimized conditions and having a 0.7 nm thick Ge layer. High positive and negative gate voltages cause the C-V curves to shift in the direction of stored negative and positive charges respectively, while no hysteresis appears at 2 V gate voltage (V_g) sweep. In the former case, charge trapping occurs through electron and hole injection from the substrate into the oxide. A gradual increase in the flat-band voltage shift (ΔV_T) with increasing V_g -sweep until 7 V is observed and ΔV_T is measured to be ~ 1.1 V. No flat-band voltage shift is observed for a reference sample prepared under similar conditions but without Ge indicating that the memory effect is Ge nanocrystals related. From the flat-band voltage shifts and the areal dot density we have estimated that approximately 2 electrons are trapped per dot for a V_g -sweep of 7 V.

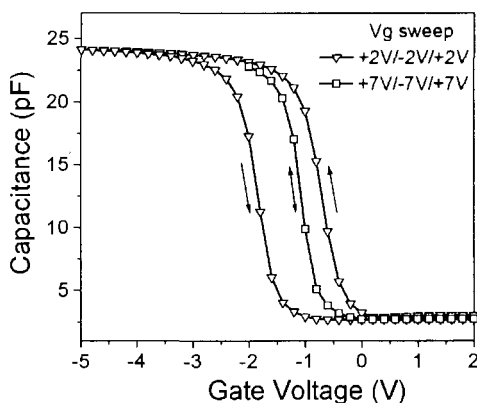


Figure 9. High-frequency C-V curves of a MOS capacitor produced under optimized conditions with a 0.7 nm thick Ge layer. A gate voltage (V_g) sweep from +7 V (inversion) to -7 V (accumulation) and from -7 V to +7 V is shown ($\blacktriangle$) by the arrow to the left and to the right, respectively. No hysteresis is observed when the sweep is within ± 2 V ($\blacksquare$).

5 Conclusion

A fabrication technique based on MBE in conjunction with optimized RTP has been demonstrated, which is capable of producing a layer of crystalline Ge-nanodots in SiO_2 of a high aerial density, uniform size distribution, and of a well defined distance from the Si/ SiO_2 interface. A significant memory effect was manifested by the hysteresis in the high-frequency C-V measurements for samples produced under optimized conditions.

Acknowledgement

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INVITED

MECHANISMS OF ISLAND VERTICAL ALIGNMENT IN Ge/Si(001) QUANTUM-DOT MULTILAYERS

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The effect of vertical ordering in superlattices of self-assembled Ge/Si(001) quantum dots was investigated by a combination of structural and optical characterizations via *in situ* reflection high-energy electron diffraction, transmission electron microscopy, atomic force microscopy and photoluminescence spectroscopy. We show that the phenomenon of vertical ordering is characterized not only by the alignment of islands along the growth direction but also by a reduction of the critical thickness in subsequent layers. The better the vertical ordering, the more pronounced the reduction of the critical thickness is observed. As a result of this finding, we demonstrate that quantum-dot superlattices in which dots having equal size in all layers can be formed. Furthermore, experiments dealing with the transformation of island shape *versus* the spacer-layer thickness reveal that preferential nucleation induced by surface roughness may be the main mechanisms responsible for the vertical ordering observed in quantum-dot superlattices.

1 Introduction

Since the first observation of the formation of defect-free three-dimensional (3D) islands in the early stage of germanium deposition on silicon, the growth of Ge/Si self-assembled quantum dots has attracted a considerable interest [1]. The carrier localization, the three-dimensional confinement, the high Ge content achieved with the heterostructures represent specific advantages for a new generation of devices [2]. However, one of the major limitations of the self-assembled quantum dots is that they exhibit broad distributions both in size and position.

It has been shown that starting from a single layer with inhomogeneous islands one can greatly improve the island size uniformity by growing multilayer structures [3]. A feature of particular interest observed in such structures is that under appropriate spacer thickness the dots in the upper layers tend to grow on the top of the buried ones, giving rise to the vertical alignment of islands along the growth direction [4]. Compared to self-assembled dots formed in a single layer where no interaction between dots could be possible due to a too large interdot distance (of about 150-200 nm in the Ge/Si system [5], for example), the feature of vertical

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ordering in multilayers may open new areas of applications such as electronically coupled quantum dots [6] and vertical transport. The mechanisms leading to such vertical ordering have been then the subject of numerous investigations [7-19]. It is now generally accepted that the driving force which leads to the vertical island alignment in QD superlattices is elastic strain fields created by buried islands and mediated by spacer layers. However, the detailed mechanisms or the manner through which such strain fields manifest or affect the nucleation of islands at the surface of the spacer layer are still not fully understood.

In this work, we investigate the effect of vertical ordering in a Ge/Si(001) multilayer structure. We have combined *structural* and *optical* characterizations, via *in situ* reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), transmission electron microscopy (TEM) and photoluminescence spectroscopy (PL), with a special attention being paid to the control of the island formation processes. The article is organized into two sections: the first section is devoted to the comprehension of the evolution of the island dimension with increasing the number of deposited layers while the spacer thickness is kept constant. The second section deals with the influence of the spacer thickness on the vertical alignment of islands in a bilayer structure.

2 Experimental

Experiments were carried out in an ultrahigh vacuum chemical-vapor deposition (UHV-CVD) system. Pure SiH₄ and hydrogen-diluted (10%) GeH₄ were used as gas sources. The system base pressure was better than 1×10^{-10} Torr while the hydride partial pressures during the growth were about 5×10^{-4} and 2×10^{-4} Torr for GeH₄ (H₂) and SiH₄, respectively. One of the advantages of our work is the use of *in situ* RHEED to precisely monitor, in real-time, the 2D-3D growth mode transition in a CVD system working at high pressures. Indeed, our RHEED gun is equipped with a differentially-pumped system, allowing us to probe the growing surface even at hydride partial pressures up to 10^{-1} Torr. More details of the experimental setup and growth conditions can be found elsewhere [20].

The Ge deposition was carried out at temperatures of 550 and 600 °C. The choice of such temperatures was guided by the fact that in this temperature range the islands in a single layer exhibit a *dome* shape, a point which is crucial for the study of the island shape transformation and will be discussed below. The Ge growth rate is about 1.5 monolayers (ML) per min. The Si deposition was carried out at 600 °C with a growth rate of about 2.5 nm per min.

The substrates were flat, *p*-type Si(001) wafers. Cleaning of the substrate surface followed the newly developed procedure utilizing the hydrogen-terminated Si(001) surface [21]. It consists of two steps: the first is a wet chemical treatment in NH₄F solution to produce an ideally dihydride-terminated Si(001) surface. The second step is heating in ultrahigh vacuum to desorb the passivating hydrogen layer at a temperature of about 450-500°C.

3 Results and discussion

3.1 Evolution of the island dimension in multilayer structures

As we have mentioned above, a general feature that has been observed in multilayers of different materials is that the island dimensions, both lateral size and height, increase when increasing the number of deposited layers [3, 4]. An increase, for example, by a factor of about three has been observed in Ref. 3 after the deposition of 20 SiGe/Si periods. From the technological point of view, such an evolution of the island dimensions may be considered as one of the main drawbacks for the application of multilayer arrays. Indeed, the size distribution is one of the main parameters, which determine the linewidth of photoluminescence peaks which is at the heart of the performances of QD-based devices.

In InAs/GaAs multilayers, Nakata *et al.* [7] have shown, from RHEED, that the InAs critical thickness in upper layers was smaller than that of the first layer. However, these authors have not clearly established whether such a decrease of the InAs critical thickness was due to the strain induced by underlying layers or surface migration of In atoms. Similar results have been observed in the Ge/Si system by Schmidt *et al.* [9, 10]. However, as such measurements were done by means of TEM microanalysis in postgrown samples, no proposal to improve the island size homogeneity has been submitted.

Fig. 1(a) shows a representative [011] cross-sectional TEM image of a multilayer consisting of 10 Ge/Si periods, the thickness of the Si spacer is 22 nm. The growth temperature is 550 °C for Ge and 600 °C for Si, respectively. The Ge deposited amount in each layer was chosen to be equal to the critical thickness determined *for the first layer*. This thickness, determined from RHEED intensity oscillations, was ~4 ML. This amount was then kept *constant* during the deposition of all upper layers. The image clearly shows that each island in the upper layers grows on the top of the ones in the lower layers, resulting in a high vertical correlation between islands. It can be also seen from the image that the islands undergo a drastic change both in size and height from the first to the third layer, and they become almost stable from the fifth layer. The average island dimensions in the first layer, ~100 nm in size and ~7 nm in height, are respectively found to increase up to ~180 nm and ~12.3 nm in the fifth layer and then remain nearly unchanged.

The PL spectrum of the corresponding sample is shown in Fig. 1(b). For comparison, we report in the lower curve the PL spectrum of a single layer. The single layer was covered with a 22 nm-thick Si cap layer, i.e. *identical* to the first bilayer of the multilayer sample. Apart from the narrow peak at 1098 meV which is attributed to the phonon-assisted recombination of the free-exciton in the Si substrate, the single-layer spectrum consists of two separate components characteristic of the Ge wetting layers (WL) and Ge islands, respectively.

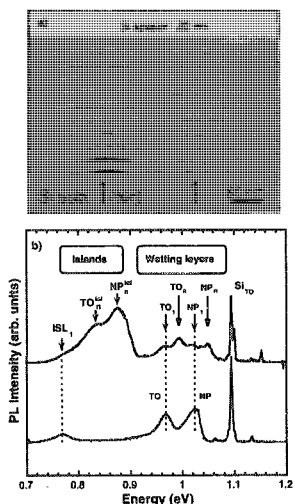


Figure 1. (a) Typical TEM image of a sample with 10 Ge/Si bilayers. The Ge coverage was chosen to be equal to the critical thickness of the first layer and was kept constant in all layers; (b) 11K-PL spectra of a single layer (lower curve) and of a 10-bilayer structure (upper curve).

The WL component is characterized by two main lines NP and TO, which are, respectively, due to the excitonic no-phonon (NP) and transverse-optical (TO)-phonon-assisted transitions of pseudomorphic Ge layers in Si [22]. The energy difference between the NP and TO lines is ~ 57 - 58 meV, which corresponds to the Si-Si optical phonon energy in Si. The emission band lying at the lower energy, of ~ 768 meV, can be attributed to Ge islands [5, 22]. The multilayer spectrum also consists of two components, but, importantly, both of them now contain two separate parts. The WL component now contains 4 main lines, denoted to as NP_1 , TO_1 , NP_n and TO_n , instead of the two ones observed in the single-layer spectrum. The NP_1 and TO_1 lines can be attributed to arise from the *first* Ge WL, while additional lines, NP_n and TO_n , can then be interpreted as arising from another Ge wetting layer, which has a thickness smaller than that of the first layer. For the island-related component, three peaks, denoted to as ISL_1 , TO_n^{isl} , and NP_n^{isl} , can be resolved after a deconvolution by using a set of three gaussian line-shaped peaks, which have their maxima at 768, 833 and 875 meV, respectively. The ISL_1 peak stems from the islands in the first layer. The other two peaks, NP_n^{isl} and TO_n^{isl} , can be attributed to NP and TO transitions of islands from the rest of the layers. The fact the island-related PL from the upper layers consists of two peaks or, in other words, the appearance of a phonon-assisted transition may be indicative of a decrease of the carrier localization inside those islands due to the increase of their sizes and heights in the upper layers.

To further clarify the existence of another type of Ge WL in upper layers, we have undertaken a RHEED analysis, by measuring the Ge critical thickness in each layer. It is now well established that the 2D growth regime is associated with the observation of streaky RHEED patterns due to reflection diffraction from a smooth crystal surface, while 3D growth is characterized by spotty patterns due to

transmission diffraction through 3D islands. The transition from 2D to 3D growth can be precisely determined by measuring the variation of the RHEED intensity of a bulk-type diffraction spot as a function of the Ge growth time and thus Ge coverage [20].

Shown in Fig. 2(a) is the evolution of the 2D-3D transition time (or the critical thickness) versus the number of the deposited layers. The upper curve corresponds to the Si spacer thickness of 22 nm while the lower one corresponding to the thickness of 2.5 nm. For $d_{\text{Si}} = 22$ nm, the Ge critical thickness, which is of 4 ML in the first layer, is found to decrease rapidly within the three first layers and reaches a stable value of 2.08 ML after the fifth layer. As a result of the RHEED analysis, the multilayer structure is found to present 5 critical thicknesses, which are of 4, 2.5, 2.25, 2.13, and 2.08 ML for the 1st, 2nd, 3rd, 4th, and the last six layers, successively.

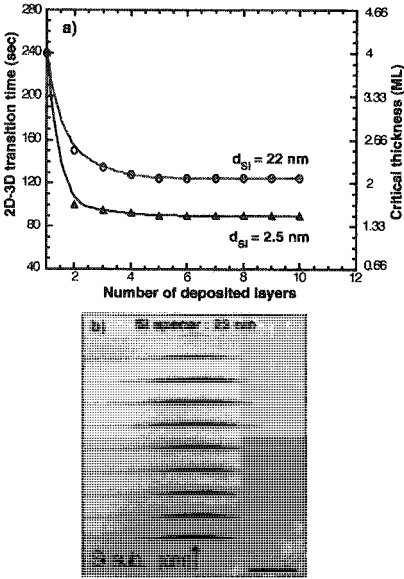


Figure 2. (a) Evolution of the Ge critical thickness as a function of the number of deposited layers in a multilayer consisting of 10 Ge/Si periods for the Si spacer thickness of 22 and 2.5 nm. The solid lines are only guides for the eyes; (b) TEM image of a sample with 10 Ge/Si bilayers in which the Ge deposited amount was no longer kept constant but adjusted with the effective critical in each layer, the spacer thickness is 22 nm.

The finding of the decrease of the critical thickness in the upper layers of a multilayer structure has brought us to a very simple idea for the realization of a multilayer structure in which the islands may have equal size in all layers. Indeed, if one does not keep the Ge deposited amount constant in all layers (equal to the critical thickness of the first layer), but adjusts this amount according to the effective critical thickness in subsequent layers, this can conduct to the formation of islands at the first nucleation stage in all layers. As a demonstration, a cross-sectional TEM image of a multilayer consisting of 10 Ge/Si periods produced with this approach is shown in Fig. 2(b). The Ge growth in each layer was stopped just after the appearance of 3D spots in RHEED patterns. The Si spacer-layer thickness was kept constant, being of 22 nm. As can be seen in this image, the islands still exhibit a

high correlation along the growth direction. An important result is that the islands have now almost equal size and height in all layers, in contrast to the case presented in Fig. 1(a) in which the Ge amount was kept constant in all layers.

What is particularly interesting is that by using this approach one can produce multilayers containing islands of uniform dimensions even when the spacer thickness is reduced down to a nanometer scale. An example on the formation of *identical* Ge islands for a spacer thickness being reduced down to 2.5 nm is presented in Fig. 3(a). The variation of the corresponding critical thickness *versus* the number of deposited layers is reported in the lower curve of Fig. 2(a). The image clearly reveals that the Ge islands have almost equal size and height in all layers. The fact that the islands within a column can have equal size and height even in very closely spaced stacked layers offers a promising opportunity for studying the electronic coupling between islands. Indeed, only in the case of having equal size, the islands within a column can have the same energy and will provide a real effect of electronic coupling.

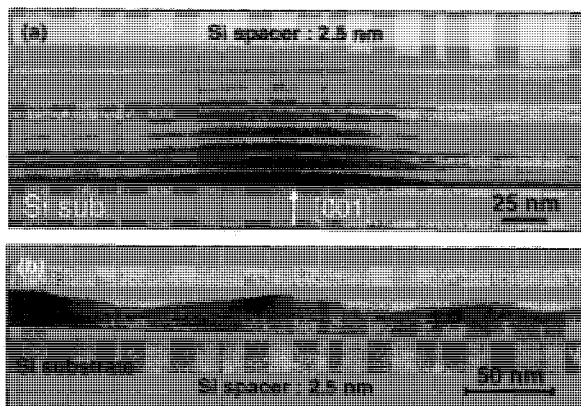


Figure 3. (a) TEM image of a 10-bilayer sample in which the Ge deposited amount in each layer was adjusted with the 2D-3D transition detected by RHEED. The d_{Si} was reduced down to 2.5 nm; (b) TEM image of a 10-bilayer structure, in which the Ge deposited amount was kept constant in all layers and the spacer thickness between adjacent islands was reduced to 2.5 nm. It can be seen that from the third layer the islands are not completely covered by Si.

To better see the importance of the effect of the reduction of the critical thickness in stacked layers in future QD-based tunneling devices, we have realized a 10-bilayer structure, in which the Ge deposited amount was kept constant in all layers. The Si spacer thickness between adjacent islands was chosen to be 2.5 nm, a value typically used in tunneling devices. It is worth noting that as the height of capped islands in the first layer is about 7 nm, the total thickness of the spacer layer is 9.5 nm. This amount was then kept constant in all layers. Fig. 3(b) shows a typical TEM of such a structure. In contrast to the image of Fig. 3(a), the present image clearly shows that the Si spacer layer is not thick enough to completely cover

the islands in upper layers. Indeed, due to the increase of the island dimensions, the Si spacer thickness between adjacent islands is found to be progressively reduced with increasing the number of deposited layers. This, in turns, contributes to an additional increase of the island dimensions in upper layers. After the deposition of three periods, the island dimensions become so large that they are not completely covered by silicon. As a consequence, the periodicity is completely lost from the fourth layer.

3.2 Mechanism of vertical ordering in multilayer structures

Starting with the aim to extract the main physical parameters, which may characterize the effect of vertical ordering in multilayers, we have investigated in a systematic manner the influence of the spacer thickness on the degree of the island vertical alignment. It is important to emphasize that such a study has been the subject of numerous investigations in different multilayer systems [4, 8-12]. However, in these works the authors have mainly used cross-sectional TEM analysis to quantify the degree of the island position alignment. While cross-sectional TEM micrographs can give a direct view on the island alignment, the analysis, which are only based on cross-sectional TEM, reveal a very large dispersion. In Ge/Si multilayers, for example, Rahmati *et al.* [12] reported a value of about 100 nm of the Si spacer thickness below which a perfect island correlation was observed while Kienzle *et al.* [8] obtained a value which is 4 times smaller than the above one. It is obvious that the presence of hydrogen in CVD experiments used in Ref. 12 could not explain this too large difference because at a growth temperature as high as 700°C the growing surface is known to be free of hydrogen.

Here, we have combined RHEED and TEM to study the effect of the island ordering. Motivated by our finding on the reduction of the critical thickness *versus* the number of deposited bilayers, we have systematically undertaken measurements of the Ge critical thickness in the second layer as a function of the thickness of the Si spacer layer. The growth temperature was 600°C for both Ge and Si. Fig. 4 shows a typical result on the variation of the critical thickness in the second layer (d_{c2}) *versus* the Si spacer thickness (d_{Si}). d_{c1} is the Ge critical thickness in the first layer, which is of 4 ML.

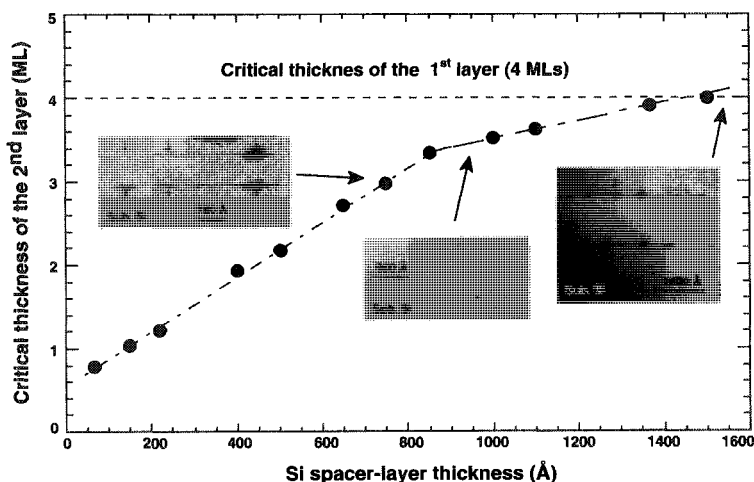


Figure 4. Variation of the Ge critical thickness in the second layer as a function of the Si spacer thickness. Note that the variation of d_{c2} can be divided into three distinct regions and described by straight lines with varying slopes represented by dotted lines. Shown in the inset are typical TEM images corresponding to the Si spacer thickness of 80, 90 and 160 nm.

As can be seen from the figure, the variation of the Ge critical thickness in the second layer (d_{c2}) can be divided into three distinct regions: the first region corresponds to Si spacer thicknesses above 150 nm, the second corresponds to a thickness between 150 and 85 nm and the third region corresponds to a thicknesses below 85 nm. In the first region, d_{c2} is equal to d_{c1} , which clearly indicates that for spacer thicknesses larger than 150 nm, the growth of the second layer is not affected by the strain field induced by buried islands. For d_{Si} below 150 nm, d_{c2} is found to decrease when decreasing the spacer thickness. It is worth noting that for very thin spacer layers, d_{c2} is reduced down to less than one monolayer of Ge. A feature of particular interest is that the reduction of the critical thickness can be described by straight lines with varying slopes. The inflexion point of the spacer thickness corresponding to the change of the slope is at about 85 nm. This value is very close to the lateral size of the buried islands, which is of 95-100 nm.

In order to see if the above behavior in the variation of the critical thickness is linked the degree of the island alignment, we have systematically undertaken TEM measurements with special attention having been paid to the spacer thicknesses at which the curve slopes change. Some representative results are shown in the inset of Fig. 4. First, it is important to emphasize that for all values of d_{Si} going up to 85 nm, TEM measurements reveal a high vertical alignment between islands along the growth direction. An example for $d_{Si} = 22$ nm was already shown in Fig. 2(b), where a high correlation between islands is observed since the second Ge layer. TEM measurements of a bilayer sample with $d_{Si} = 55$ nm (not shown here) confirm that the islands remain highly vertically correlated. For a bilayer with $d_{Si} = 80$ nm, i.e. just before the change in slope of the $d_{c2}(d_{Si})$ curve, TEM image clearly reveals

that a high vertical alignment between islands is still preserved (Fig. 4). In the second region corresponding to d_{Si} increasing from 85 to 150 nm, the vertical correlation was found to become progressively reduced when d_{Si} increases. A TEM image corresponding to $d_{Si} = 90$ nm, i.e. just after the change in the $d_{c2}(d_{Si})$ curve slope, is shown in Fig. 4. The islands in the second layer are now not directly formed above the buried ones but slightly laterally shifted. Finally, when d_{Si} becomes larger than 150 nm, a value from which d_{c2} becomes the same as d_{c1} , the island arrangement becomes completely random, as illustrated in the TEM image with $d_{Si} = 160$ nm.

The above TEM and RHEED analyses provide a nice coherence between the island vertical alignment and the variation of the critical thickness in the upper layer. These results clearly indicate that the phenomenon of vertical ordering is characterized not only by the alignment in island positions but also by a reduction of the critical thickness in the upper layer. To further understand the influence of the strain fields of buried islands on the nucleation of islands in the second layer, we performed another series of experiments with the aim to investigate the evolution of the island shape. The idea is to see how the nucleation of islands in the second layer involves when the spacer thickness passes through the three above regions defined from the variation of the critical thickness. Because Ge/Si islands exhibit a large variety of surface morphology [23-25], the choice of the island morphology on the *starting surface* appears judicious. Indeed, depending on growth conditions, Ge/Si islands can be elongated {105} faceted hut clusters [23] or consist of both square-based pyramids and multifaceted domes [24, 25]. We first investigated the island formation in a single layer as a function of the growth temperature and the GeH_4 flux and we have chosen the growth parameters, so that the islands in the first layer have all a dome shape. A typical morphology of such a surface is presented in Fig. 5, which indicates that all islands in the first layer have a dome shape.

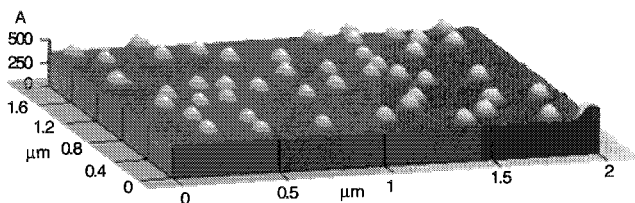


Figure 5. A three-dimensional AFM image of a Ge/Si single layer grown in the temperature range between 550 and 600 °C. The GeH_4 partial pressure was about 5×10^{-4} Torr. The surface exhibits islands all of which have a dome shape.

Displayed in Fig. 6 are AFM images of the surface in the second layer corresponding to three regimes of island correlation. While the starting surface only consists of domes, the AFM image of the second layer in the highly correlated region exhibits islands, all of which have a square-based pyramidal shape. These pyramids are oriented along the [110] directions and bounded by {105} facets. This

indicates that the strain field of buried islands which propagates through the Si spacer layer significantly modifies the nucleation process of upper islands. Pyramids are systematically observed for Si spacer thicknesses increasing up to 85 nm, i.e. up to the change in slope of the critical thickness curve. For Si thicknesses corresponding to a reduced correlated region, i.e. for Si thickness varying from 85 to 150 nm, pyramids and domes coexist. An example corresponding to the Si thickness of 90 nm is shown in Fig. 5. Finally, for Si thicknesses above 150 nm, i.e. in the uncorrelated region, only dome islands are observed in the second layer (an example for the Si thickness of 160 nm is shown in the inset of Fig. 5). This observation indicates that the system has now returned to its original situation where the growth of a second layer becomes independent of the buried layers.

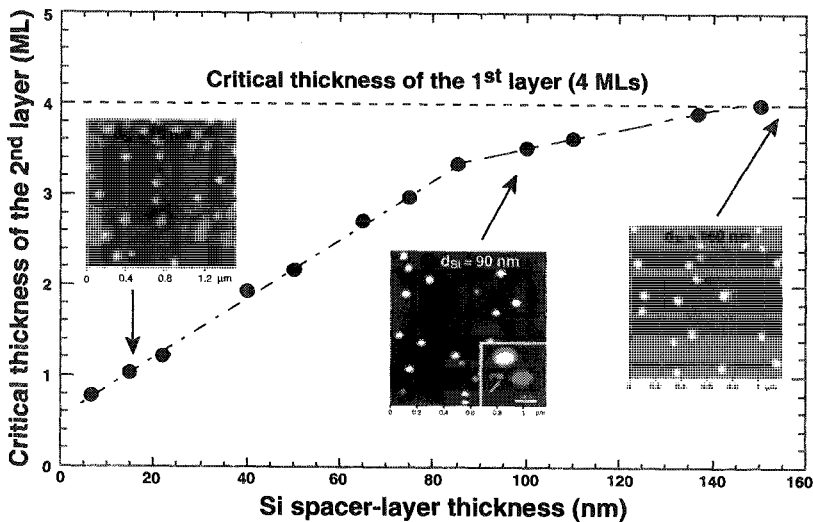


Figure 6. Variation of the Ge critical thickness and typical AFM images of islands in the second layer measured in three regions of island correlation: 15 nm, 90 nm and 160 nm.

The driving mechanisms for the island vertical correlation have been the subject of extensive studies over the past years. Because the buried islands produce a nonuniform strain field at the surface of the spacer layer, i.e. the regions above the islands are tensely strained while the regions in between islands remain compressed, exciting models have treated the island distribution at the spacer layer surface by considering the effect of such a strain field on surface diffusion [4] or on island nucleation [3]. Recent calculations have taken into account the effect of the elastic anisotropy of the materials [16], the surface energy [18] or the elastic interaction between the buried islands with newly deposited ones [19]. However, in all of the above models it was assumed that the surface of the spacer layer becomes *perfectly* flat before the deposition of a new layer. From the experimental point of view, this

assumption has never been established. Fig. 7 shows a zoom around a square-based pyramid of the AFM image corresponding to the Si thickness of 15 nm.

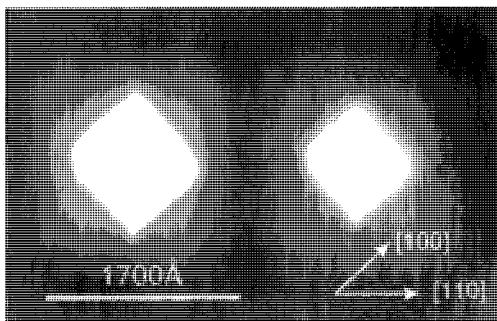


Figure 7. A zoom around square-based pyramids of AFM image shown in Fig. 6 corresponding to the Si spacer of 15 nm.

A striking feature that can be seen from this image is that whereas the wetting-layer surface between islands is flat, each pyramid is found to be sitting on a square-base region, which has a roughness amplitude of about 4-5 Å. These regions have a dimension of about 170 nm x 170 nm and are oriented along the [110] directions. The dimension of this region is almost twice larger than the lateral size of the buried islands, which may give a rough estimate of the extension of the strain field of the buried islands. The pyramids have a density of the same order of magnitude as that of the first layer, confirming therefore that each pyramid grown on the top of a buried island. It should be emphasized that such roughening is not observed on single layers exhibiting square-based pyramids as well as single layers covered by dome-shaped islands. The ensemble of these results suggests that the formation of pyramids in the second layer stems from preferential nucleation associated with surface roughness induced by the elastic strain fields of buried islands. In other words, preferential nucleation associated with surface roughness appears to be the dominant mechanism, leading to vertical ordering in superlattices of self-assembled quantum dots.

4 Conclusion

To summarize, we have demonstrated that the phenomenon of vertical ordering is characterized not only by the alignment of islands along the growth direction but also by a reduction of the critical thickness in subsequent layers. The better the vertical ordering is, the more pronounced the reduction of the critical thickness will be. Such a decrease of the Ge critical thickness can be explained by elastic strain fields induced by buried layers and mediated by the spacer layers. We have shown that when the Ge deposited amount is no longer kept constant in all layers as frequently carried out in typical experiments but adjusted according to the *effective*

critical thickness in subsequent layers, multilayers of self-assembled quantum dots in which dots have uniform dimension in all layers can be produced. Furthermore, by analyzing the transformation of the island shape *versus* the thickness of the spacer layer, we show that preferential nucleation induced by surface roughness may be the main mechanism responsible for the vertical ordering observed in quantum-dot multilayers. It is believed that stacked layers having *identical islands* represent promising systems for a study of electronic coupling and vertical transport between islands.

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INVITED

ENHANCED LUMINESCENCE OF LANTHANIDES FROM XEROGELS IN POROUS ANODIC ALUMINA

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The paper summarizes recently investigated properties of a structure "microporous xerogel/mesoporous anodic alumina", doped with erbium, terbium and europium. An enhancement of green, red and infrared photoluminescence (PL) from the structure associated with intra-transitions of trivalent lanthanides in xerogels is discussed.

1 Introduction

Mesoporous matrices impregnated with sol-gel derived solid films, so-called xerogels, reveal interesting optical properties. By fitting the size a mesoporous cage and adjusting chemical composition sols, the sol-gel method allows to fabricate films with thickness of hundreds nanometers possessing a wide range of refractive index and highly doped with different optically active ions in a xerogel host. A structure "mesoporous silicon/erbium doped silica xerogel" exhibits both a strong visible luminescence and 1.53 μm light emission caused by $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition in Er^{3+} [1, 2]. The titania xerogel/artificial opal structure comprises a solid 3D photonic band-gap material [3], leading to synthesis of inverse opals [4] and light-emitting structures with the emission spectrum within the photonic bandgap [5]. However, among artificial porous materials we consider the structure "microporous xerogel/mesoporous anodic alumina" as one of the most promising for optoelectronics.

Anodizing of aluminum under certain conditions produces self-organized regular periodic structures with hexagonal cells and controlled sizes of the pores from 10 through 500 nm [6, 7]. Unique porous films with thickness up to 200 μm with an insignificant variance of the pore diameter oriented perpendicularly to the planar surface were fabricated [8, 9]. Porous anodic alumina (PAA) is a relatively transparent material and could be fabricated on the substrates transparent in the wide spectral range (Fig. 1 [10]) that makes it attractive for optical excitation of diverse luminescent inclusions.

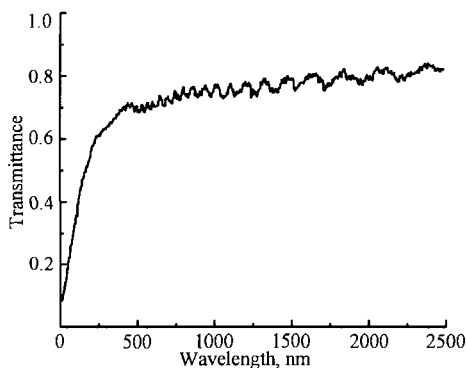


Figure 1. Transmission spectrum of 5 μm thick porous anodic alumina film on quartz substrate grown during anodizing of Ta/Al structure in electrolyte of phosphoric acid.

This paper summarizes peculiarities of synthesis and optical properties of the microporous xerogel/PAA structure highly doped with Er, Tb and Eu. The enhancement of PL emission from these dopants in the structure is discussed.

2 Experimental

PAA was fabricated either on aluminium foils (UMIST, Manchester) or Al deposited onto silicon or quartz substrates (BSUIR, Minsk) by anodizing in electrolytes based on phosphoric or oxalic acids [10-21]. The average pore size was ranged from 40 to 120 nm in diameter depending on the electrolyte. Different sols have been developed to fabricate SiO_2 , TiO_2 , Al_2O_3 , In_2O_3 , SnO_2 and other xerogel films doped with Er, Tb and Eu. Typical concentration of sols was about 20 – 30 mg/ml. Er, Tb, Eu nitrates were dissolved in a homogeneous phase with ethanol and water to fabricate a xerogel film containing from 10 to 70 wt.% of lanthanide oxides. The sols containing the lanthanides were deposited by spinning at a rate ranging from 2000 to 3000 rpm. Sometimes we used the dip coating technique [16], but spin coating deposition was found to be more efficient for fabrication of the structures exhibiting enhanced PL of the lanthanides. Sequential coatings were fabricated by deposition of each layer followed by heat treatment.

3 Results and discussion

3.1 Fabrication of xerogels in the pores of anodic alumina

Fabrication of xerogels within the pore volumes after spin-on deposition of a sol followed by drying was confirmed by different experimental techniques. First, it was revealed in BSUIR (Belarus) by SIMS-analyses of 3 μm thick PAA spin-on

coated with erbium-containing silica sol followed by heat treatment [13]. Xerogel was observed and identified more evidently on the walls and at the bottom of the pores at UMIST (UK) using TEM and EDX-analysis of cross-sections of 2-30 μm thick structure PAA/titania doped with Tb – Fig. 2 [15, 17]. It was also observed on the walls of PAA with SEM of the cleaved edge of the 5 μm thick structure PAA/titania doped with Eu, fabricated on silicon.

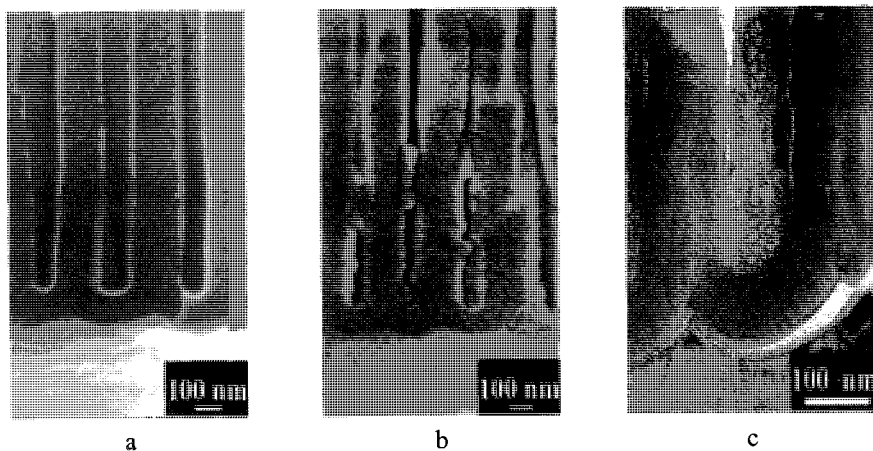
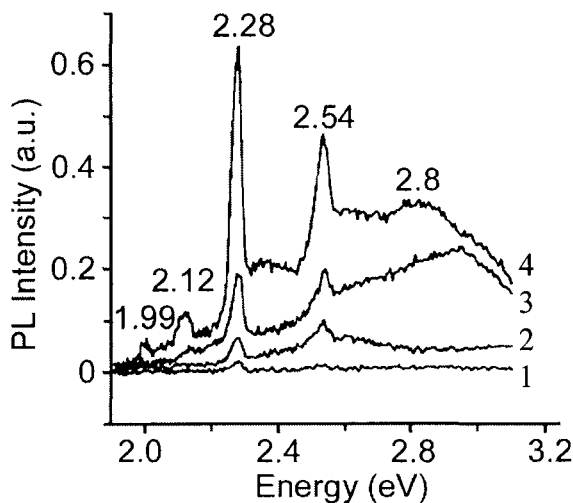


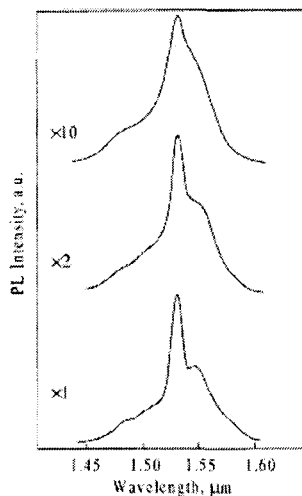
Figure 2. SEM (a,b) and TEM (c) micrographs of the structure xerogel/anodic alumina: (a) - as anodized anodic alumina film of 5 μm thick fabricated on Si, (b) - after one spin-on deposition of Eu-doped titania xerogel; (c) – ultramicrotomed sections of the terbium-doped alumina xerogel/PAA structure of 30 μm thick. Bottom of the pore was filled with terbium-doped alumina xerogel after five spin-on depositions.

3.2 *Enhanced luminescence of lanthanides*

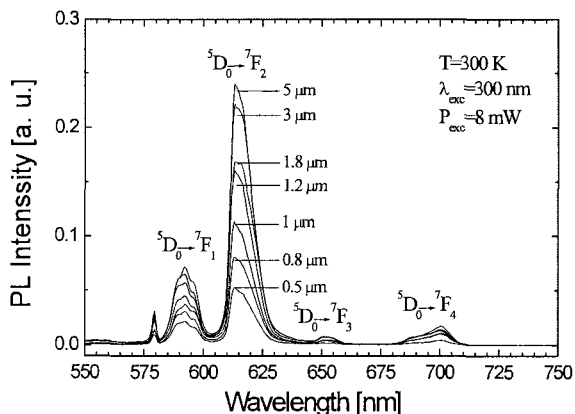
The first results related to strong room-temperature 1.53 μm emission from xerogel/anodic alumina structure we have obtained in 1994 and reported in 1995 [11, 12]. This work was proposed in our group following to our research with spin-on films for diffusion in semiconductors [1, 22, 23]. Initially, 2-3 μm thick PAA and Er doped silicagel derived from $\text{Si}(\text{OC}_2\text{H}_5)_4$ were employed [11]. Further, we used titania xerogels instead of silica as a host of optically active lanthanides. Strong enhancement of Er, Tb and Eu PL from xerogel films confined in mesoporous anodic alumina was observed in comparison with spin-on films fabricated on monocrystalline Si.



a



b



c

Figure 3. Room temperature PL of (a) - Tb, (b) - Er, and (c) - Eu doped titania xerogels fabricated on silicon and porous anodic alumina. PL spectra of Fig. 3(b) correspond to one (upper curve), five (medium curve) and ten (lower curve) deposition of erbium-doped xerogel layer.

Fig. 3 summarizes the systematic enhancement of room temperature PL of Tb, Er and Eu observed due to deposition of the lanthanide-doped titania xerogels in the alumina pores and also the further enhancement due to pore filling with these xerogels and due to increase the thickness of a PAA layer [15, 16, 18]. Very weak PL emission with a maximum at 2.28 eV was detected after fabrication of a single layer spun onto the silicon wafer (Fig. 3(a), curve (1)) [15]. Building up the xerogel film on silicon by spin-on deposition of ten layers (2) reveals a weak PL emission with maxima at 2.28 and 2.54 eV. By comparison, the PL intensity is significantly greater in a sample containing only one layer of xerogel deposited on porous alumina (3). It is significantly increased in the case of an identical porous alumina

structure containing ten spin-on layers (4), and bands are now observed with maxima at 2.54, 2.28, 2.12 and 1.99 eV. These bands are attributed to the $^5D_3 \rightarrow ^7F_4$, $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$ and $^5D_4 \rightarrow ^7F_3$ transitions in Tb^{3+} ions, respectively.

PL at 1.53 μm , corresponding to the transition between the first excited state $^4I_{13/2}$ and the ground state $^4I_{15/2}$ of Er^{3+} ions in xerogel was detected at room temperature after fabrication of one erbium doped silica [13, 14] or titania [16] xerogel layer onto PAA of 2-3 μm thick. An example of such luminescence is given by Fig. 3(b) for titania xerogel. Fabrication of the single erbium-doped silica or titania xerogel layer onto flat surface of monocrystalline silicon reveals no PL emission at 1.53 μm [1, 11, 16]. Er-related PL from the sample coated ten times is about one order of magnitude greater than for the sample coated in one step.

PL spectra of the samples of PAA of different thickness coated with Eu-containing xerogel are presented in Fig. 3(c) [10]. Four optical bands corresponding to $^5D_0 \rightarrow ^7F_j$, ($j = 1 \dots 4$) of Eu^{3+} transitions with the maximum at 617 nm ($^5D_0 \rightarrow ^7F_2$) are well resolved in the spectra. About a fivefold increase in integral PL intensity is observed upon the increase of the porous layer thickness from 0.5 to 5 μm .

The Tb- and Eu doped xerogel/ PAA structures exhibit green and red light emission, respectively, visible to the naked eye at any temperature in the range of 10–300 K.

3.3 Intriguing properties of xerogel/PAA structures

Various sol-gel derived films in PAA exhibit some intriguing optical properties. Recently performed analysis of transmission and PL excitation spectra of Tb-and Eu-doped xerogels fabricated onto flat glass substrates PAA-structures suggests that in these structures excitation of lanthanides could be realized by the three mechanisms (i) directly, (ii) through xerogel matrix, and (iii) due to the multiple scattering of exciting light by the matrix of mesoporous anodic alumina.

An increase of lanthanides PL could be observed due to: (i) an increase of the number of xerogel layers within the volume of anodic alumina pores [15, 16], (ii) an increase of the concentration of lanthanide ions with respect to the concentration of the host oxide in the same sol [14, 15, 17], (iii) an increase of the thickness of the film [15, 18] and (iv) tailoring of the parameters of the structure depending on the emission range of the incorporated lanthanides.

Er, Tb and Eu PL in the structure xerogel-PAA increases with the concentration of lanthanides in the xerogel film. Concentration quenching of lanthanides PL or cooperative up-conversion effects have never been observed from our samples. The enhancement of PL with concentration and with the number of xerogel layers we associate with the increased absorption of the exciting light.

The structures alumina xerogel/PAA doped with Tb demonstrated very low thermal PL quenching which is untypical for lanthanide-doped films [17]. The thermal quenching does not exceed a factor of two within a temperature range from 10 to 300 K. It is much lower in comparison with (i) Tb-doped titania xerogel, (ii)

Tb-implanted thermally grown silicon dioxide film, and (iii) Tb-doped alumina xerogels fabricated onto monocrystalline silicon. Thus, the terbium-doped alumina xerogel/PAA structure was proposed as a basis for green room-temperature luminescent images [17].

The deposition of ten erbium-doped titania xerogel layers onto PAA results in the two-fold narrowing of FWHM of the erbium related band at $1.54\ \mu\text{m}$ in comparison with the samples coated with five layers, i.e. from 30 to 15 nm. The values of FWHM observed at room temperature are comparable with those obtained for erbium-implanted in SiO_2 (13 nm), SR-350 resin (21 nm) or porous silicon (23 nm) [16]. Probably, building of ten xerogel layers produces an erbium-doped xerogel of improved quality, revealing the narrower optical band at $1.53\ \mu\text{m}$.

Finally, the fabricated periodic structures could exhibit the photonic band gap effect, revealing an enhancement of the lanthanide-related emission at the direction to the detector and its inhibition in other directions parallel to the plane surface of a sample. This effect can contribute to the explanation of the enhanced PL of lanthanides from the structure and recently observed anisotropy of Eu PL from titania xerogel/PAA structure, as given by Fig. 4 [10].

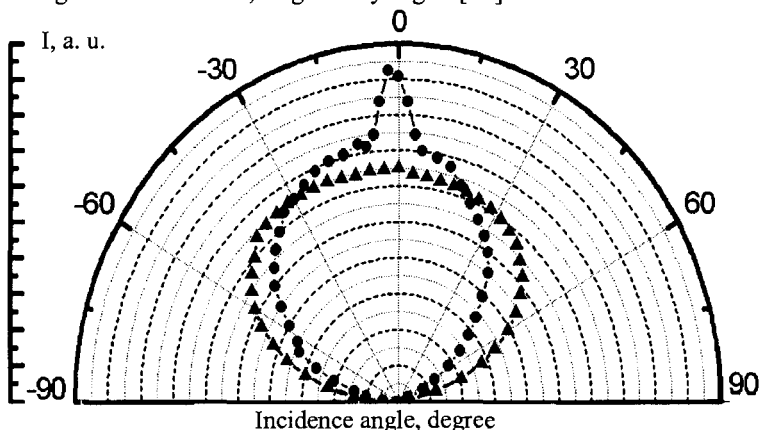


Figure 4. Indicatrices of Eu^{3+} PL from the structure titania xerogel/PAA of $30\ \mu\text{m}$ thick (●) and from the same xerogel on monocrystalline silicon (▲).

4 Conclusion

Further development of the electrochemical and sol-gel processes leads to fabrication of the efficient light emitting film structures based on microporous xerogels in mesoporous anodic alumina. We observed room-temperature green and red electroluminescence from Tb- and Eu doped In_2O_3 and SnO_2 xerogels in PAA. We expect that the efficiency of these light-emitting structures could be increased

by improving the parameters of both: (i) the conductive transparent xerogels, like antimony-doped tin oxide [24], tin-doped indium oxide [25]; (ii) PAA, exhibiting the pronounced photonic band-gap effect in the visible range.

Acknowledgements

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INVITED

ADVANCED SCANNING PROBES AS APPLIED TO SELF ORGANIZED ORGANIC SYSTEMS

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Nanoscale sciences are strongly driven by scanned probe techniques, which allow us to investigate and manipulate surfaces down to the atomic scale. While the imaging capabilities of techniques such as STM, SFM, SNOM etc. dominated the application of these methods at their early development stages, the physics of probe-sample interactions, and the quantitative analysis of elastic, electronic and magnetic surface and transport properties are becoming now of increasing interest.

Recent progress in dynamic force microscopy/spectroscopy (SFM/SFS) as applied to polymers, and molecular layers such as OMBE-films and LB-films is briefly reported here and illustrated by Figs. 1-6.

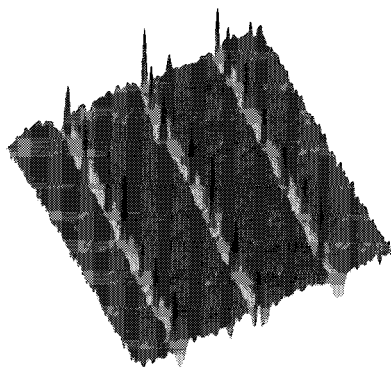


Figure 1. Au₅₅ nanoclusters deposited in a nano-channel lattice [4].

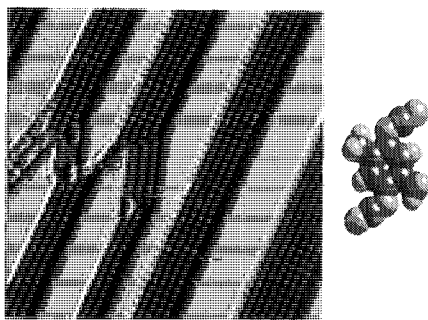


Figure 2. DCNQI molecules on Ag (775) organic molecular beam epitaxy (OMBE).

Dynamic force spectroscopy (DFS) was introduced [1] allowing us to understand quantitatively dissipative and non-dissipative processes in dynamic force microscopy [2]. Using a combined experimental and computer simulation technique it is possible to reconstruct force/distance curves without using any model potentials and parameters. This method opens the perspective to extract material parameters such as atomic densities of the surface investigated as well as local elastic properties

of the sample. In addition, energy dissipation occurring during high resolution imaging can be evaluated [3]. An instrumental improvement based on a modified electronic feed back control unit ('Q-control') allows us to compensate the hydrodynamic background damping that is sizeable for dynamic SFM operations in air and liquids. Effectively, the quality factor of the SFM cantilever beam can be increased, resulting in a sensitivity that is comparable to that of an SFM cantilever driven under vacuum conditions. Thus, soft organic materials such as organic layers and biological systems can be imaged without deterioration. This AFM-technique was applied to supermolecular periodic layers [4] and biological structures [5].

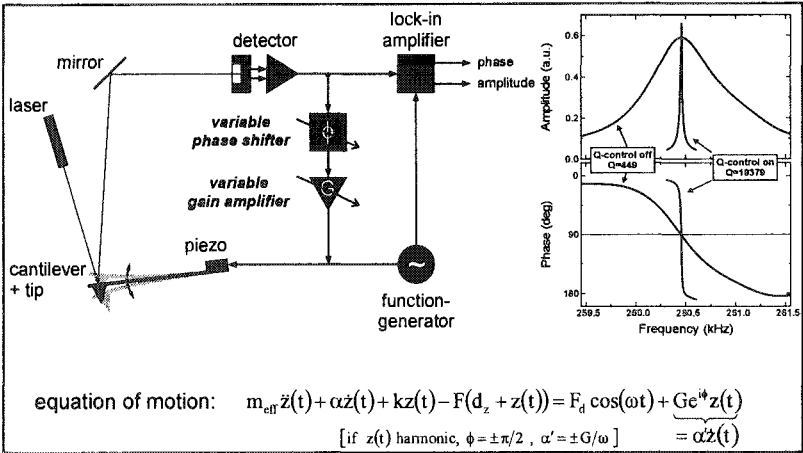


Figure 3. Scheme of Q-controlled dynamic AFM with Q-control [3].

Scanning near field optical microscopy (SNOM) opens the perspective to apply optical imaging and spectroscopy techniques to soft matter far below the classical diffraction limit. A use of the novel SNOM technique [6,7] based on an aperture less probe provides a lateral optical resolution in the range of 1-10 nm.

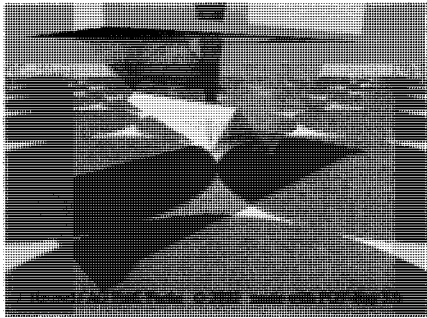


Figure 4. Set up of a combined STM/SNOM based on the tetrahedral tip [6].

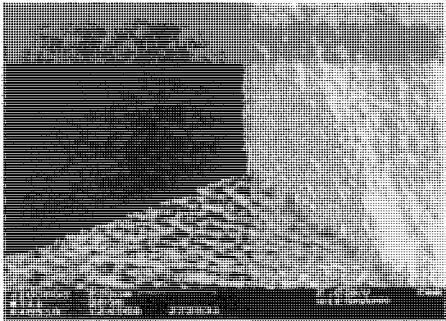


Figure 5. SEM image of a metal coated tetrahedral tip.

Fluorescence images

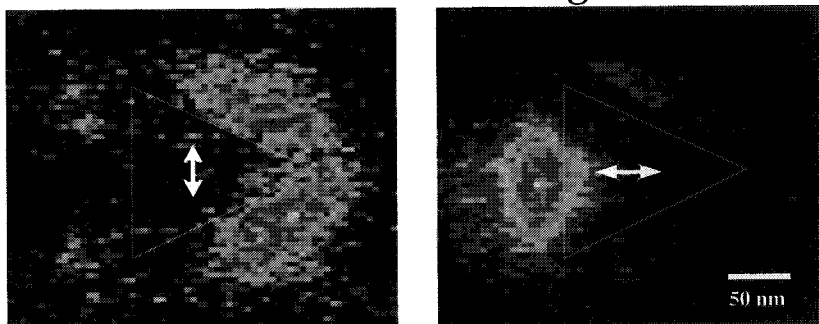


Figure 6. Triangular aperture SNOM probe excited with two different polarization states. With polarization shown on the left side two maxima of the electric field occur. Rotating the polarization by 90 degrees virtually only one maximum occurs [7].

The geometrical shape of a novel aperture like SNOM probe influences the imaging properties of photonic nanostructures. By using triangular shaped aperture probes a selection of the position of the electrical field strength maximum at the rim of the metallic aperture can be achieved by adjusting the polarization direction [7].

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NEW PRECISE NANOSTRUCTURES: SEMICONDUCTOR SHELLS AND THEIR WELL ORDERED ARRAYS

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An overview of our original works in the field of precise cylindrical nanoshells (nanotubes, nanospirals, and nanorings) self-formed from III-V single crystals and Si/GeSi heterofilms and from metal-semiconductor, metal-metal and hybrid films is presented. New results are described on the formation of spatially periodic structures, open and closed single-crystal 3D nanoshells of various shapes with the minimum radius of curvature of ~ 1 nm, and also on assembling these shells in even more complex architectures.

1 Introduction

Precise nanostructuring is a cornerstone problem in solid-state nanotechnology. Its successful solution would allow a breakthrough in a number of fields in science and industry. Nature is known to be capable of producing molecules and molecule-like objects with unprecedented precision. There are monoatomic-thickness nanoshells (carbon nanotubes and fullerenes) among these objects. These nanoshells are considered to be promising building blocks for future electronics [1]. Recently we proposed a new method of precise fabrication of three-dimensional (3D) micro- and nano-shells of cylindrical geometry (tubes, scrolls, ring, spirals) by self-rolling of strained heterofilms [2-19].

2 Results and discussion

The method for fabricating nanotubes from GaAs/InAs strained heterostructures [2-4] is schematically illustrated by Fig. 1. The diameter D of self-formed tubes depends on the thickness d of the initial heterofilm and on the value of the elastic stress in it. This diameter therefore can be defined precisely in an MBE process. For a heterofilm made using two layers with identical thickness d , we have $D \approx d/(\Delta a/a)$, where $\Delta a/a$ is the lattice mismatch between the two layers. The high quality of MBE-grown heterostructures makes it possible to obtain several centimeter long rolled tubes with diameters as small as 3 nm and with atomically smooth and uniform tube walls. From the above structures not only tubes, spirals and rings [2-4] but also other various shells formed by locally released films can be prepared [5,9].

The possibility of fabricating nanoobjects has been demonstrated using a series of epitaxial structures grown on GaAs, InP, InAs, Si substrates [2-19] (Fig. 2-4).

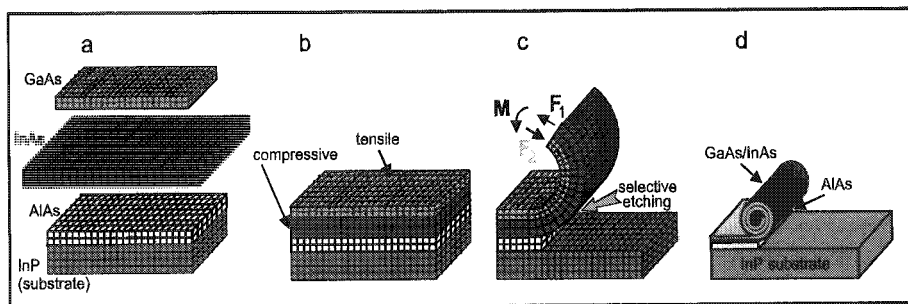


Figure 1. Schematic representation of the method used to form free-standing bent or rolled-up several monolayer thick films. (a) Free 2ML-thick InAs and GaAs layers with naturally mismatched lattice constants ($\Delta a/a = 7.2\%$); (b) matching of the layers at the interface between them during their epitaxial growth; (c) bending of the GaAs/InAs monolayers film after its partial detachment from the substrate during selective etching of the underlying AlAs sacrificial layer; d – self-rolling of the GaAs/InAs bifilm in a tube-scroll during further selective removal of the sacrificial layer.

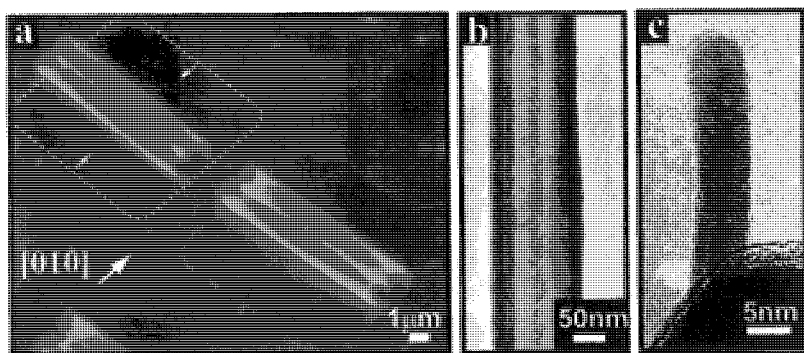


Figure 2. SEM and HRTEM images of InGaAs/GaAs nanotubes rolled-up from bi-layered films. (a) Two scrolls after their collision at the end of their formation process; (b) Initial-bifilm thickness 4ML GaAs + 4ML $\text{In}_x\text{Ga}_{1-x}\text{As}$ ($x = 0.6$); (c) 2ML GaAs + 1ML InAs.

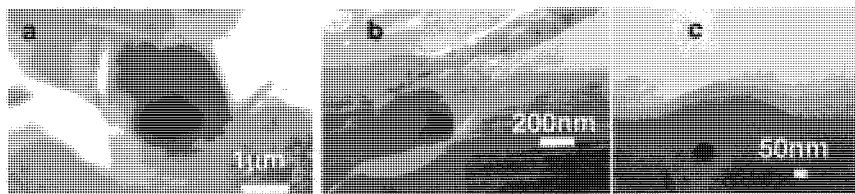


Figure 3. SEM images of overgrown tubes.

At the next stage of our studies, we developed a new robust method for rolling lithographically defined planar strained heterofilms in preset directions to obtain 3D-free-standing shells of even more complex geometry and properties (Fig. 4). Precise micro- and nanotubes, and also other precise nanoshells can be used as building blocks for more complex device structures. Like molecules, such building

blocks can travel over the substrate surface and interact with each other, forming desirable complex configurations (Fig.2 a).

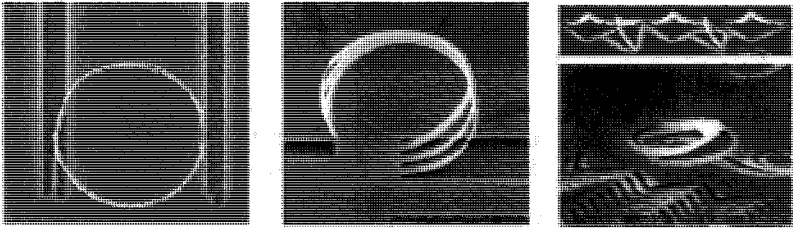


Figure 4. SEM images of ultra-thin film structures (a) a ring with vertically aligned nanowalls, (b) bended strips (cantilevers); (c) arrays of needles; (d) Archimedean spiral, spiral-like strip.

These films open new opportunities in studying properties of semiconductor interfaces. For instance, 2 ML-thick single-crystal InAs/GaAs films in which all molecules may be considered as occupying simultaneously free-surface and hetero-interfacial sites, display unusual chemical and mechanical properties such as: (i) stability against oxidation [2,4], (ii) bright manifestation of surface-tension forces in their elastic characteristics, and (iii) “flexible” room-temperature bonding giving rise to a single-crystal monolith [2,6]. The stress in a rolled film substantially affects the properties of the film material [10]. The computations revealed spatial separation of electrons and holes in nanotube walls (Fig. 5).

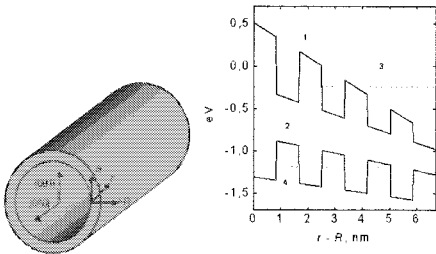


Figure 5. Schematic view of an InAs/GaAs nanotubes (left) and energy positions of the conduction- (1) and valence-band (2) edges in the tube walls, and the position of the electron (3) and hole (4) energy levels.

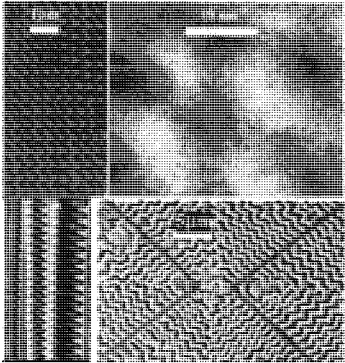


Figure 6. Periodically corrugated structures.

Solid state nanoshells with a rich variety of shapes can be obtained with the above-described technology [5,9,12,13,15,17-19]. The simplicity of the proposed method, its applicability to a broad class of materials and, finally, its compatibility with the mature integrated-circuit technology allows to anticipate its wide practical applications in the future. Using InGaAs/GaAs and SiGe/Si strained heterofilms, we showed a possibility of forming 3D shells that may be used for creating various

microelectromechanical systems [4,7-19]. Additionally, assembling shells of various shapes into structures offer a new route in fabricating complex architectures which the industry demands today.

Acknowledgments

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CHARACTERIZATION OF NANOCRYSTALLINE SILICON FILMS BY BEAM INDUCED CURRENT IN THE SCANNING TUNNELING MICROSCOPE

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Electrically active regions of nanocrystalline silicon (nc-Si) films have been investigated by using a SEM/STM combined instrument. STM constant current images reveal a cell structure in the nc-Si which is also observed in the remote electron beam induced mode of the STM. The STM-REBIC contrast indicates the existence of space charge regions at the cell boundaries.

1 Introduction

Electronic characterization of the structural features of nc-Si is of interest due to the important role of the defects that appear in the surface of the nanocrystals, or in the interface between the nanocrystals and an oxide or amorphous phase, on the luminescence properties of this material [1]. The REBIC (remote electron beam induced current) mode in the SEM has been successfully applied in the past to investigate electrically active defects in high resistive semiconductors [2] while STM-REBIC has been only occasionally used to image defects in materials such as CuInSe₂ [3], diamond [4] or sintered zinc oxide [5]. The signal generation in REBIC is mainly due to the presence of space charge regions and it provides direct evidence for electrically active barrier structures [6]. The previous results have shown the capability of the STM-REBIC technique to characterize electrically active defects with a very high spatial resolution. In this work, REBIC mode of operation in a STM is used to image electrically active barriers in nc-Si films with a resolution of about 10 nm. To complement the STM study CITS measurements have been also performed.

2 Results and discussion

Amorphous silicon films, with a thickness of about 2 μm , were obtained by LPCVD on p-type silicon wafers at 570°C and pressure of 0.4 Torr. In order to obtain

nanocrystalline silicon (nc-Si), the amorphous films were implanted with boron ions with energy of 100 keV and dose of 10^{15} cm^{-2} as discussed elsewhere.

Some of the samples were annealed at 650 °C for one hour. The microscopic measurements were performed in a combined SEM/STM system based on a Leica 440 SEM operating under a vacuum of 1×10^{-6} Torr. The small size of the STM enabled it to be mounted on the SEM specimen holder. Mechanically sharpened Pt-Ir wires were used as probe tips for tunneling experiments. The STM was used in the conventional constant-current mode, in the current imaging tunneling mode (CITS) and in the STM - REBIC mode. For STM-REBIC mode, two ohmic contacts were provided by small HgIn dots on the sample surface connected to Au or Pt-Ir wires. The tunnel tip was located on the region between the contacts and the current was measured at room temperature with a Keithley 428 current amplifier.

The nanocrystalline silicon films were formed by crystallization of the amorphous matrix during boron implantation and consist of nanocrystals with an average size of about 10 nm arranged inside a cell structure with sizes around 200 nm, as previously found by X-ray diffraction and STM techniques [7]. Fig. 1 shows the constant current image and the corresponding STM-REBIC image of the 10^{15} cm^{-2} doped sample. In the constant current image (Fig. 1a) the surface cell structure is observed while a contrast associated with space charge regions present in the cell boundaries is observed in the STM-REBIC image (Fig. 1b). In Fig. 1c the line profile of both REBIC signal and the topography across the dark line pictured in Fig. 1b are shown. The width of the cell boundary revealed in the STM-REBIC image is about 20 nm.

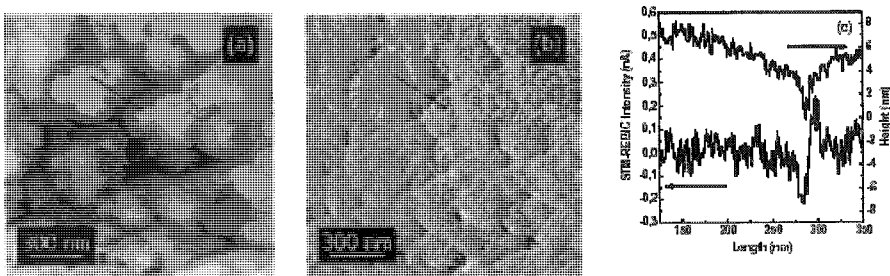


Figure 1. (a) STM constant current image of the nc-Si implanted with a dose of 10^{15} cm^{-2} ; (b) corresponding STM-REBIC image and (c) topography and REBIC profile of the line indicated in (a) and (b).

At constant current STM-REBIC and CITS images were also acquired after thermal treatment of the nc-Si films. The topography shows the same features as in the as-implanted samples while the STM-REBIC images do not show any contrast. The contrast of the cell boundaries in the CITS images is also removed after the annealing of the films. These results indicate that the thermal treatment induces an enhancement in conductivity of the samples due to a recrystallization process and a change in the cell boundaries defect distribution and structure.

3 Conclusions

The present results show the capability of the STM-REBIC technique to image electrically active defects or regions in nc-Si films. The spatial resolution achieved in the STM-REBIC mode was about 20 nm. The signal profiles obtained in the boundaries of the cell structure observed in nc-Si are in agreement with an electrically charged boundary model. Annealing of the samples leads to the disappearance of the STM-REBIC as well as the CITS contrast.

Acknowledgements

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PULSED LASER ANNEALING OF GERMANIUM NANOCLUSTERS IN SILICON

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Modification of Ge nanoclusters in Si matrix by ruby laser pulses has been studied. Energy density of irradiation was near melting threshold of Si surface. The decrease of the nanocluster in size and the partial relaxation of stresses are observed. More considerable changes occur by multipulse irradiation. Ge nanoclusters are transformed into the clusters of $\text{Ge}_x\text{Si}_{1-x}$ solid solution.

1 Introduction

A study of formation and modification of Ge quantum dots (QD) in Si is the actual problem due to perspectives to apply Ge/Si nanostructures in optoelectronic devices [1]. To obtain nanoclusters with specified properties it is important to control sizes and density of Ge QDs. The modification of Ge nanocluster sizes is reached [2,3] by variation of temperature and growth rate, change of interfacial mechanical stresses, creation of buffer layers, insertion of impurities as nucleation centres, and stimulation of island growth by ion beams. In this paper, modification of Ge QDs by pulsed laser radiation was studied by Raman spectroscopy.

2 Experimental

Ge/Si nanostructures were formed by molecular beam epitaxy. A buffer layer with 150 nm thickness was grown on Si substrate doped by P (resistivity $5 \Omega/\text{cm}^2$) at 600°C . 4, 8 or 10 monolayers were grown with Ge nanoclusters covered by Si layer with the thickness of 150 nm. The samples were then irradiated by ruby laser beam with the pulse duration of 80 ns. Inhomogeneity of energy distribution in the laser spot (6 mm in diameter) did not exceed $\pm 5\%$. Energy density in a pulse was about

1 J/cm^2 . That corresponded to the melting threshold of crystalline Si [4]. Number of pulses was 1 or 10. Spectra of Raman scattering (RS) excited by Ar laser radiation (514.5 nm) were registered at room temperature in the back scattering geometry. Other details of experiments and calculations were described elsewhere [5].

3 Results and discussion

There is a peak from 300 to 312 cm^{-1} in the RS spectra of as-fabricated nanostructures (Fig. 1, A-C). This peak is caused by optical oscillations of Ge-Ge bonds. It is shifted to the higher frequency than in the bulk Ge due to compression stresses. This shift is much bigger than the 'low frequency' one caused by quantum-dimensional effects. RS peaks observed in the range from 350 - 450 cm^{-1} correspond to optical oscillations of Ge-Si bonds in the heterostructures.

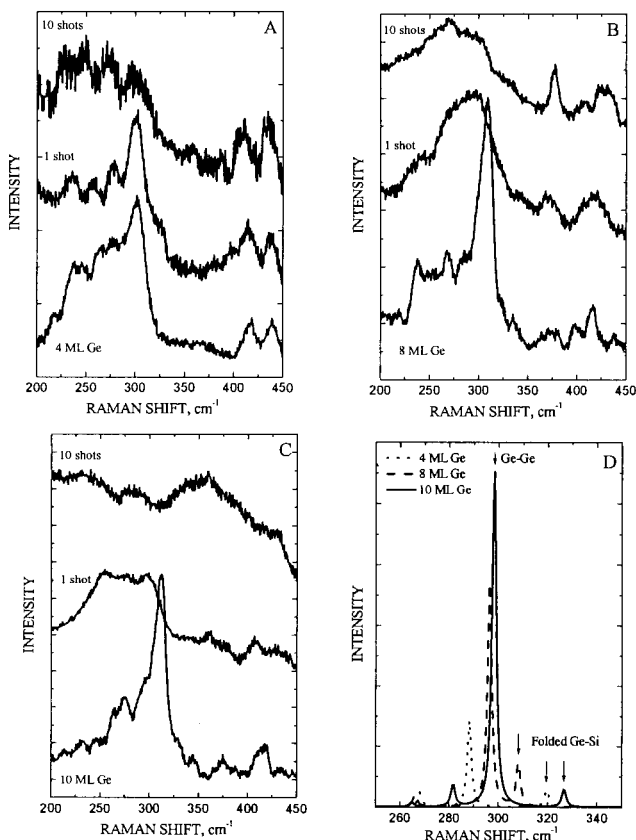


Figure 1. Experimental (A-C) and simulated (D) Raman spectra of nanostructures under study.

The calculations of eigen frequencies of RS and eigen vectors of oscillations were carried out within the Born-von-Karman model. The power constants were

fitted using experimental dispersion of bulk Ge phonon modes [6]. RS spectra were obtained by the model of additive polarizability of bonds [7]. The calculated RS peak corresponding to oscillations on Ge-Ge bonds shifts to the lower frequencies with a decrease of effective thickness of Si (Fig. 1 D).

From the comparison of spectra of as-fabricated and irradiated samples, it is possible to conclude that the irradiation by a single pulse results in drastic changes of the nanocluster structure, in particular for the samples with 8 and 10 monolayers of Ge. The peak corresponding to Ge-Ge bonds is broadened and shifted to lower frequencies. It can be explained by a decrease of QD size, increase of the size dispersion and relaxation of mechanical stresses in it. More drastic changes are observed in the spectra of samples irradiated by 10 laser pulses. The clusters of solid solution $\text{Si}_x\text{Ge}_{1-x}$ are formed in this case.

4 Conclusion

It have been established that the single laser pulse changes properties of Ge QDs. Modification of their size, composition and mechanical stresses takes place. More considerable changes occur under irradiation by 10 laser pulses when Ge clusters are transformed in to clusters of $\text{Ge}_x\text{Si}_{1-x}$ solid solution.

Acknowledgement

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REGULAR STRUCTURES ON SILICON SURFACE FORMED UNDER COMPRESSION PLASMA FLOW

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Formation of regular structures on silicon surface subjected to compression plasma flows is described. Results of numerical simulation are presented. Possible mechanisms of the structures formation are discussed.

1 Introduction

It was found for the first time [1,2] that the action of compression plasma flows on silicon surface causes the regular nanoscale structures. Previous attempts to obtain such structures on silicon surface failed despite of the variety of methods used. The interest to this effect is triggered not only by technological application, but also by investigation of the basic physical processes giving rise to an appearance of such highly oriented periodic patterns.

In our experiments, the compression plasma flows were obtained in a quasi-stationary plasma accelerator known as the magnetoplasma compressor (MPC) [3,4]. Plasma flow in the MPC is compressed due to the interaction between longitudinal component of current swept away from an accelerating channel and intrinsic azimuth magnetic field. The presence of "swept-away" current in the plasma flow is a consequence of magnetic field freezing into plasma.

The paper presents experimental investigation of regular structure formation and numerical simulation of melting and crystallization processes on the silicon surface exposed to compression plasma.

2 Experimental setup

The compression plasma flows were obtained using a gas-discharge MPC of compact geometry powered by a capacitive storage ($C_0=1200\text{ }\mu\text{F}$) and operating at initial voltages, U_0 , 3-5 kV. The MPC operated in a residual-gas regime wherein the pre-evacuated accelerator chamber was filled with nitrogen to a preset pressure (100-1300 Pa). The discharge duration in the MPC amounts to 120 μs , and the peak value of discharge current depending on initial parameters of the discharge ranges from 70 to 100 kA.

Under these conditions, a compression plasma flow of 6-10 cm long and 0.7-1 cm in diameter forms at the outlet of the MPC discharge device. The compression flow remains stable for about 80 μs ; thereafter it starts to diverge in a half-angle of 5 to 15°. The plasma velocity in a compression flow is in the range of $(4\text{--}7)\cdot 10^6\text{ cm/s}$, depending on initial parameters of the MPC. The concentration of charged particles in a maximum compression zone is as high as $(5\text{--}10)\cdot 10^{17}\text{ cm}^{-3}$, and the temperature of electrons attains 1-3 eV [3,4].

Monocrystalline silicon samples ($10\times 10\times 0.28\text{ mm}^3$) of (111) and (100) crystallographic orientations were mounted at an axis of the system normally to compression flow at distances of 6–16 cm from the tip of MPC discharge device. The surface microrelief of the silicon samples was examined with high-resolution scanning electron microscopy (SEM).

3 Results and discussion

Incidence of compression plasma flow on the silicon surface causes a shock-compressed plasma layer to form. The energy absorbed by silicon depending on the sample location ranges from 5 to 25 J per pulse, which corresponds (in our experimental conditions) to an increase in power density of plasma flow from $0.5\cdot 10^5$ to $3\cdot 10^5\text{ W/cm}^2$. In its turn, the density of charged particles in plasma varies from 10^{18} cm^{-3} at the maximum contraction to 10^{16} cm^{-3} in the area of compression flow divergence. Under these conditions, the impact pressure developed by incident plasma flow on the silicon surface ranged from 10 to 30 bar.

As a result of the compression plasma flow action on the sample, highly oriented periodic structures are formed on the silicon surface (Fig. 1, a-c). The structure fragments measure 100-800 nm in diameter and 50-100 μm in length. Application of steady external magnetic field ($B=0.1\text{ T}$) causes the surface structures diameter to decrease and their surface density to enhance.

Remarkable is the presence of drop-shaped structures at the tips of cylinder-like fragments (Fig. 1, b-c). Similar structures are inherent in well-known vapor-liquid-solid (VLS) mechanism of crystal growth. If this is the case, the copper particles entering the compression flow due to a weak erosion of the MPC copper electrodes

can be the centers of the drops growth. In addition, it is worth to note the presence of sporadic unusual clamshell-like structures on the silicon surface (Fig. 1d).

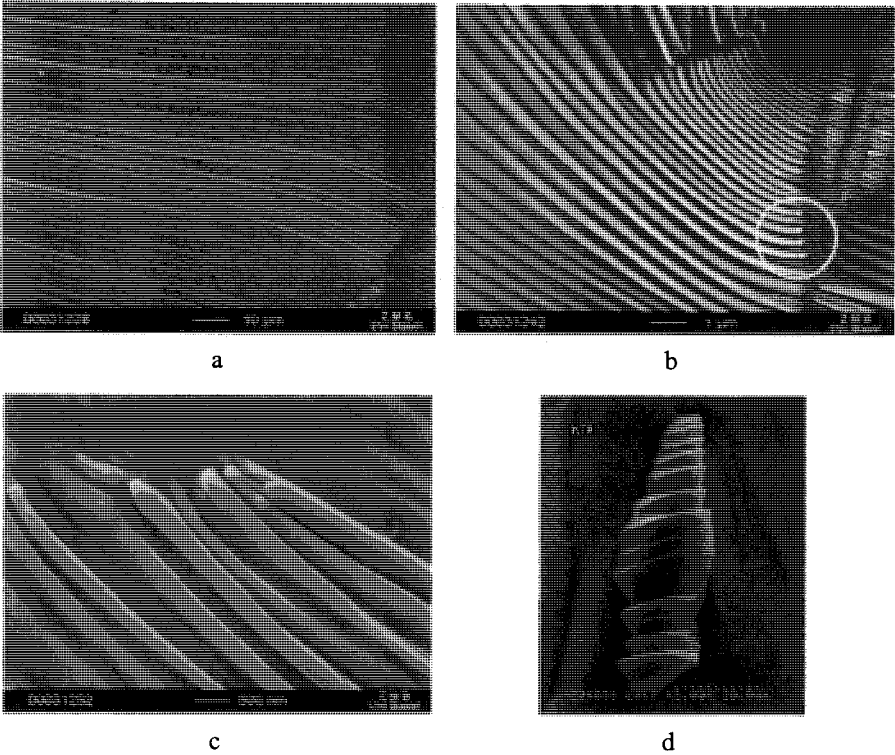


Figure 1. SEM images of surface structures on silicon samples.

To describe the processes accompanying interaction of compression plasma flow with a sample surface, the numerical model of monocrystalline silicon melting and crystallization was developed taking into account kinetics of phase transformations based on the Kolmogorov equation. It was supposed that both melting and crystallization take place as a result of homogeneous nucleation through the two-dimensional mechanism of layer-by-layer growth. Two types of boundary conditions were considered: one with assignment of boundary energy flow and another with assignment of boundary temperature.

As results of numerical simulation show, within several microseconds after the onset of plasma flow action with power density reaching $W=10^5\text{-}10^6\text{ W/cm}^2$, melting of near-surface layer begins, and the two-phase zone propagating into the bulk is formed. The overheating value at the melting front reaches 40 K. In the course of the plasma flow action, the front of two-phase zone propagates into the sample to a depth of 3-10 μm depending on the pulse form and boundary

conditions. As the power density on the sample surface decreases, the two-phase zone boundary stops propagating. The process of crystallization begins at a maximal depth of the zone penetration. For maximal pulse power density $\sim 10^6 \text{ W/cm}^2$ and action duration $\sim 100 \text{ }\mu\text{s}$, the monocrystalline silicon crystallization stops within $\sim 300 \text{ }\mu\text{s}$ after the action onset.

4 Conclusion

Formation of observed structures can be caused by energetic action of compression flow on the surface. It results in the fast heating and melting of the surface layer, development of thermoelastic stresses, and plasma spreading over the surface both under the pressure of compression flow and the gradient of plasma parameters in shock-compressed plasma layer. The crystallization of molten silicon provides fast cooling and high temperature gradients. These processes occur in the presence both of magnetic fields induced by the “swept-away” currents of compression flow, and of current loops (vortices) originating due to deceleration of magnetized plasma at the sample surface.

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NANOSCUPTOR SOFTWARE FOR FABRICATION OF SPATIAL STRUCTURES IN CRYSTALS

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It is a synthetic introduction to NanoSculptor software for a laser system, which is used for the tree-dimensional objects forming in “micro” and “nano” scales. The paper introduces the aspects, connected with the choice of programmatic environment, shows the possible methods of the formed objects discretization and depicts the topic of algorithms which operate the positional coordinate system.

1 Introduction

Today laser technologies get more and more distribution in material processing [1]. The technologies based on the applying of laser radiation in the manufacturing of elements of micro- and nano-electronic take now a special place among them.

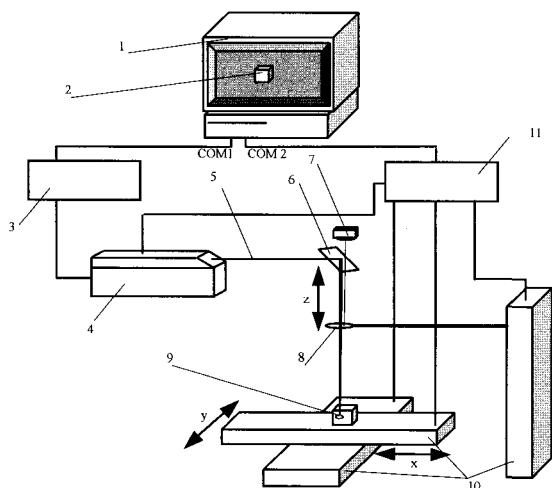


Figure 1. A sketch of the laser nanowriting machine.

The structure of laser machine for forming of 2D-, and 3D objects in transparent materials (like glass, and other transparent dielectrics), which was jointly developed by JE “Lotis TII” and Laboratory of Mathematic Modeling and

Information Technologies of Belarusian State University of Informatics and Radioelectronics, is shown on Fig. 1. It consists of personal computer (1) with specialized software, laser system (4), which includes optic units (5)-(8), laser controller (3), coordinate system (10) with processing object (9), and controller of coordinate system (11). This laser machine was successfully used to form dotted 2D and 3D micro-objects with a pulse laser. Topological possibilities of machines of such type in full measure depend on the used laser, as well as on the software, which includes a set of algorithms for coordinated control of laser and coordinate system.

2 Software for object laser forming

The preparation of two-dimensional objects is realized by means of typical graphic programs, e.g. Corel PhotoPaint, Adobe PhotoShope, etc., taking into consideration the condition, that the prepared picture must be saved in standard, black-and-white BMP file for Windows. Besides, one can prepare files, which will be converted by system, in STL binary size as well as in CAD systems size – the files with DXF widening (extension). Three-dimensional objects are prepared with 3D StudioMAX pack in version at least 2.6. The software should possess specially written scripts (“Divide Curves”, “Divide Meshes”, “Export Data”), which transform an object into layers, on which, in its turn, points are brought upon, regarding the condition of assurance of suitable distance between layers and the points which create the object.

The program NanoSculptor steers the process of 3D and 2D images' forming. It was created on the platform of language C++ under Win 32 API (Application Programming Interface) and with the libraries of MFCL class (Microsoft Foundation Classes Library), which belong to Microsoft Windows. There is a possibility of using the object classes, which create program windows and make possible the creation of menu functions, dialogue windows, as well as saving of created data. MFCL library possesses the object structure, for that very reason it is easy to adapt the accessible classes to the realization of programmatic assignments, creating the elastic code written by programists, which gives new technological possibilities, realized by the operating system.

The modeled object in three surfaces (XY, XZ, YZ) as well as the isometric image or the perspective view is introduced on the computer screen. There is a possibility of the parameters changing of the prepared earlier 3D image in the following spheres:

- changing of the size and the possibilities of object location in any point of worked material,
- a turn according to any axis with given earlier angel,
- pointing of the exact center, regarding the condition of similar distance from the external points, which create the object from the walls of the worked dielectric.

For steering of laser system, NanoSculptor software is connected with the positional coordinate system (axis XYX), which parameters are influenced on.

3 Discretization process of objects formed by laser system

The only problem of the suitable algorithm choice of discretization is the size and quantity fitting of points, which qualitatively have to copy the modeled earlier object. NanoSculptor uses three methods for this: 1) discretization methods of the object division on sections, 2) discretization methods which is based on the algorithm of triangle filling by points, 3) discretization by means of parallel bunches.

The first method applies standard operations from 3D StudioMax program. It takes that an object consists of sections, which determine the fact, that it is introduced as a row of complex closed contours. In relation to every section the analysis of the curve is presented in result of cutting curve, which is in the further stage brought near by triangles.

The discretization methods, based on algorithm of the triangles filling by points, is founded also on one of the methods, which is used in 3D Studio MAX. The received object is reflected by the triangles. The points are put in every of received triangles. Thanks to this the filling of contour is preformed. The advantage of the method is the high speed, in comparison to the introduced previously method. In spite of all the algorithm also possesses certain drawbacks. One of them is the fact, that every triangle is separately filled by points, what in geometrical structure can appear by concentration of points on the line, which joins the neighboring triangles between them. The second inconvenience appears for big areas and these areas are imaged by very small triangles. In spite of introduced inconveniences, it is however the fundamental algorithm for receiving of the first approximate images.

4 Conclusion

Taking into consideration the aspects concerning the software creation for steering the forming process of three dimensional objects it is apparent that software shall attend high criterions and be able also to couple with assignments, which are brought to the devices, using laser bunch for the object forming in “micro” and “nano” scale.

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RAPID THERMAL PROCESSING OF POROUS SILICON FOR THE STRUCTURE STABILIZATION

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Rapid thermal processing (RTP) of porous silicon (PS) is discussed to stabilize the PS structure. 1 μm thick PS layers were subjected to RTP with incoherent light pulses of second and millisecond durations. PS lattice parameters relative to the lattice parameters of a crystalline Si in the direction perpendicular to the wafer surface have been studied by X-ray double-crystal diffractometry. PS lattice is shown to be scarcely affected by light pulses of millisecond durations. At the same time RTP with light pulses from the second duration range was demonstrated to expand the PS lattice parameter considerably. PS lattice deformation should be taken into account in deciding on RTP regimes for processing of the structures containing PS layers.

1 Introduction

Porous silicon (PS) is one of the nanoscale modifications of silicon. There are various approaches to PS producing that are now in use. The technique most generally employed today is known as wet anodization of a crystalline silicon. With this technique, yield parameters of porous material (porosity, pore size and shape, interpore distance) may be readily varied by anodization regimes. However, it is well known the problem of the PS stability influencing the physical properties of the PS layers. PS instability is conditioned by very large specific surface area of the porous material.

A number of studies has been attempted to stabilize porous silicon: low-temperature oxidation in a controlled way [1-3], surface modification of silicon nanocrystallites by chemical [4] or electrochemical [5] procedures etc. Rapid thermal processing (RTP) is thought to be a shortcut method of the PS stabilization for a number of purposes. However, there is no data about RTP influence on the PS structure. Therefore, the study of lattice deformations of PS layers after RTP is of great interest. In the present work, X-ray double-crystal diffractometry was used to measure lattice deformations of PS after RTP of millisecond and second durations.

2 Experimental

Flat n^+ -type (100) Si wafers doped with antimony up to $4 \cdot 10^{18} \text{ cm}^{-3}$ were used as initial substrates. Curvature radii of the Si wafers were measured to be more than

300 m. Uniform 1 μm thick PS layers were formed by anodization in the 12% HF aqueous solution at the current density of 20 mA/cm^2 . The fourth-order reflection of $\text{CuK}\alpha_1$ radiation from (100) plane was recorded by an X-ray double-crystal diffractometer to set PS lattice parameters relative to lattice parameters of a crystalline Si wafer in the direction perpendicular to the wafer surface with an accuracy of $5 \cdot 10^{-6}$. Then the samples were subjected to RTP with incoherent light. One part of the samples was subjected to the light irradiation from halogen lamps for 3–10 s. Others were processed with the irradiation from xenon arc lamps providing much shorter pulses (the pulse duration used was of $2.5 \cdot 10^{-2}$ s at the power density of 20–30 $\text{W} \cdot \text{s}/\text{cm}^2$). After RTP, the changes in curvature radii and PS lattice parameters were studied by the above procedures.

3 Results and discussion

It has been found experimentally that PS ageing in air stabilizes the PS surface [6]. This is associated with the native silica on the PS surface. With RTP, high temperatures should enhance the silica growth providing rapid passivation of the PS surface with oxygen.

Two types of RTP used in our experiments differ considerably in the exposure time, incident irradiation absorption by the PS/Si structure, heat distribution in the wafer, and as a consequence in the extent to which RTP changes the PS structure.

90% of radiation from xenon arc lamps falls in the range of the wavelengths less than 1 μm . It is absorbed by the surface PS layer. The irradiation pulse duration in the millisecond range creates a thermal flux regime of the treatment, and with this RTP, temperature profiles are determined by heat diffusion from the radiation-absorbing regions. Radiation spectrum of halogen lamps lies in the visible and near IR range and the pulse duration of irradiation is within the range of seconds. Processing at these conditions corresponds to the heat balance regime and provides a uniform temperature distribution in the wafer [7].

Fig. 1 shows X-ray diffraction rocking curves for the as-prepared PS samples and the samples exposed to RTP. The peak from the initial PS layer is located at the left of the basic peak from the crystal silicon substrate indicating that the lattice parameter of the PS layer, measured normal to the surface, is greater than that of the Si substrate. The angular shift $\Delta\theta$ between the two peaks is directly related to the perpendicular component of the mismatch $\Delta a/a$ between porous and single silicon through the relation:

$$\Delta a/a = -\Delta\theta / \lg \theta$$

where a is the lattice parameter of the substrate, Δa is the difference between lattice parameters of PS and silicon, θ is the Bragg angle.

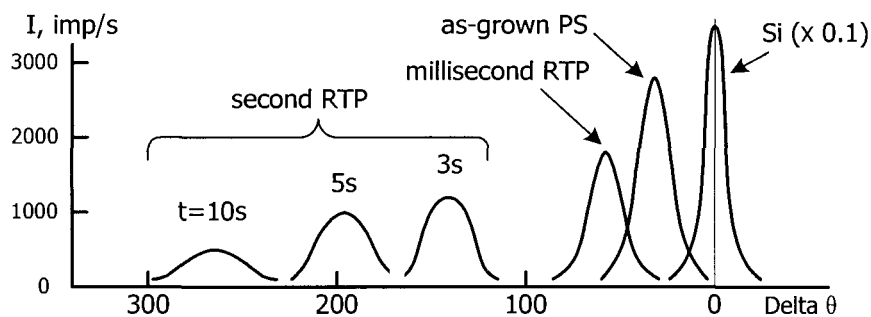


Figure 1. X-ray double crystal rocking curves for PS layers.

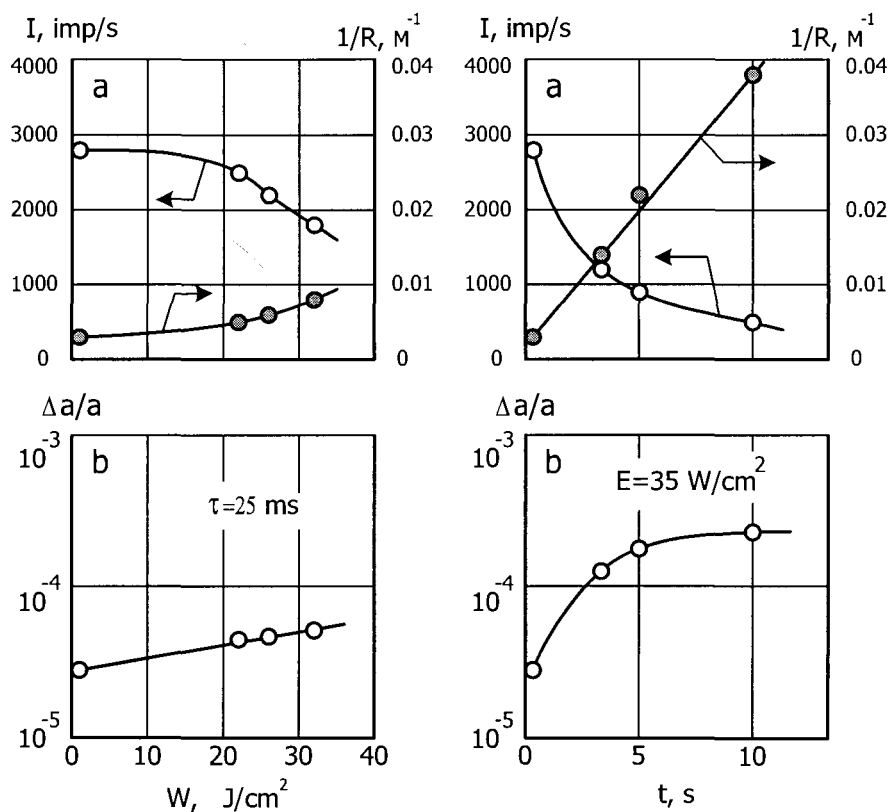


Figure 2. Energy dependences of I and $1/R$ (a), and $\Delta a/a$ (b) for millisecond RTP.

Figure 3. Time dependences of I and $1/R$ (a), and $\Delta a/a$ (b) for second RTP.

RTP by light pulses of millisecond duration resulted in the slight shift of the diffraction peaks from PS further to the left (a slight expansion the lattice parameter) while RTP by light pulses of second duration led to the considerable shift of the diffraction peaks from PS much far to the left (Fig. 1). In the latter case, the longer is the RTP time, the more considerable is the shift.

The change of the diffraction peak intensity I , the wafer curvature $1/R$ and mismatch between porous and single silicon lattice parameters $\Delta a/a$ as a function to the pulse energy density during irradiation with light pulses in the millisecond duration range is shown in Fig. 2. The change of above parameters versus pulse duration for RTP with light pulses in the second duration range is shown in Fig. 3.

Referring to Figs. 2 and 3, RTP with light pulses of second durations expands the PS lattice parameter considerably. At the same time PS lattice is seen to be scarcely affected by light pulses from the millisecond duration range. These data correlate well with the data for silicon oxidation at RTP [8]. The natural silica growth was found to be enhanced by incoherent light exposure of the pulse duration from the second range only. So, we conclude that the PS surface is oxidized at RTP with light pulses. The thickness of silica increases with the processing time. PS oxidation shows itself in the lattice parameter expansion and in the wafer deformation (increase of the wafer curvature). PS lattice deformation should be taken into account in deciding on RTP regimes for processing of the structures containing PS layers. At the same time, RTP with light pulses from the millisecond duration range leave the PS surface unoxidized. This may be taken into consideration at the PS RTP in air.

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NANO-SCALE SURFACE REPLICATION BY POLYMER LAYERS: SPM AND X-RAY INVESTIGATIONS

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We report results of nano-scale surface replication by thin polymer layers. The surfaces of deeply polished Si plates were used as etalon surfaces for the replication. AFM investigations showed that polymer layers replicate the surface of etalon samples fairly well. The X-ray reflectivity measurements showed that the half-width and peak values of the spectral dependences for X-ray mirrors grown on combined glass-polymer substrates practically coincided with those for mirrors on Si etalon substrates.

1 Introduction

Polymer materials find a wide application in replication technologies for producing structures with submicron elements of intricate shapes and for nano-scale surface replication [1-4]. They show considerable promise for smoothing out the surface roughness to obtain good-quality inexpensive substrates used in fabrication of X-ray optic components [5,6]. In this work, the features of silicon wafer surface replication by polymers were studied by atomic-force microscopy (AFM) and X-ray reflectometry (XRR) with a view to applying this replication technique to produce smooth polymer-glass combination substrates to be used in multilayer X-ray mirrors.

2 Experimental methods

Glass plates varying in the surface roughness were used as model substrates in our experiments. The roughness was smoothed out by replication of supersmooth etalon surfaces of polished Si wafers. For replicate layers we used thin films of acrylic anaerobic adhesives and photopolymer compounds.

The surface roughness of etalon samples, glass substrates and polymer replicas were investigated with "Solver" atomic-force microscopes (NT MDT company, Zelenograd, Russia). The AFM measurements data were used to construct dependence of the rms roughness σ on a frame size, which characterizes the surface roughness on a varying scale.

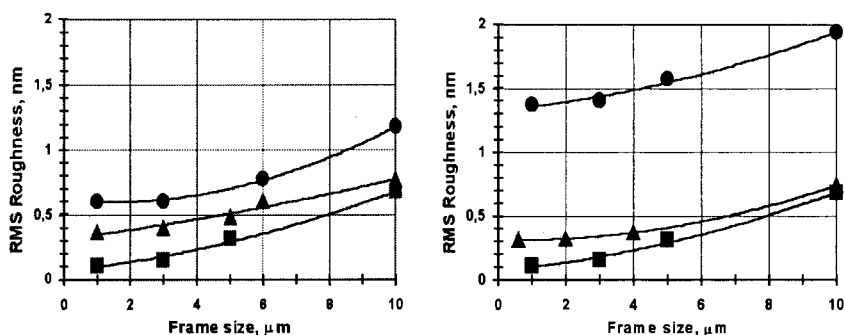


Figure 1. Scale dependences of rms roughness σ for etalon Si surface (■), glass substrates (●) and polymer replicas of Si surface (▲): (a) and (b) are the results of AFM measurements for glass substrates with an average: ~ 1.5 nm and low: ~ 0.7 nm roughness, respectively.

The angular and spectral dependences of X-ray reflectivity were studied with “DRON-3” X-ray diffractometer ($\lambda = 0.154$ nm) and X-ray reflectometer designed in IPM RAS on the basis of a RSM-500 spectrometer-monochromator (4–50 nm wavelengths).

3 Results and discussion

We have carried out a series of experiments for replication of a Si wafer surface by polymer films on glass substrates. The substrates differed in the surface roughness as ~ 0.7 nm and ~ 1.5 nm (according to the XRR data). The AFM measurements have revealed parameter σ for a polymer replica surface to be practically independent of the original roughness of the glass, its governing factor being the roughness of the etalon surface. The value of σ for the polymer layer was about 0.3–0.5 nm over an 1–5 μm area. The difference in the roughness between the polymer replica and the original silicon surface was measured to be ~ 2 nm.

We conducted direct comparative AFM studies on the conjugated areas of the etalon surface and polymer film. As etalon surface in these experiments we used a photolithographically prepared silicon grid. The results of the study (Fig. 2) show the polymer replica surface to be a high-fidelity reproduction of the etalon surface nanoscale relief features. Minimal lateral dimensions of the replicated features, considering the finiteness of the probe sizes, come to about 30 nm.

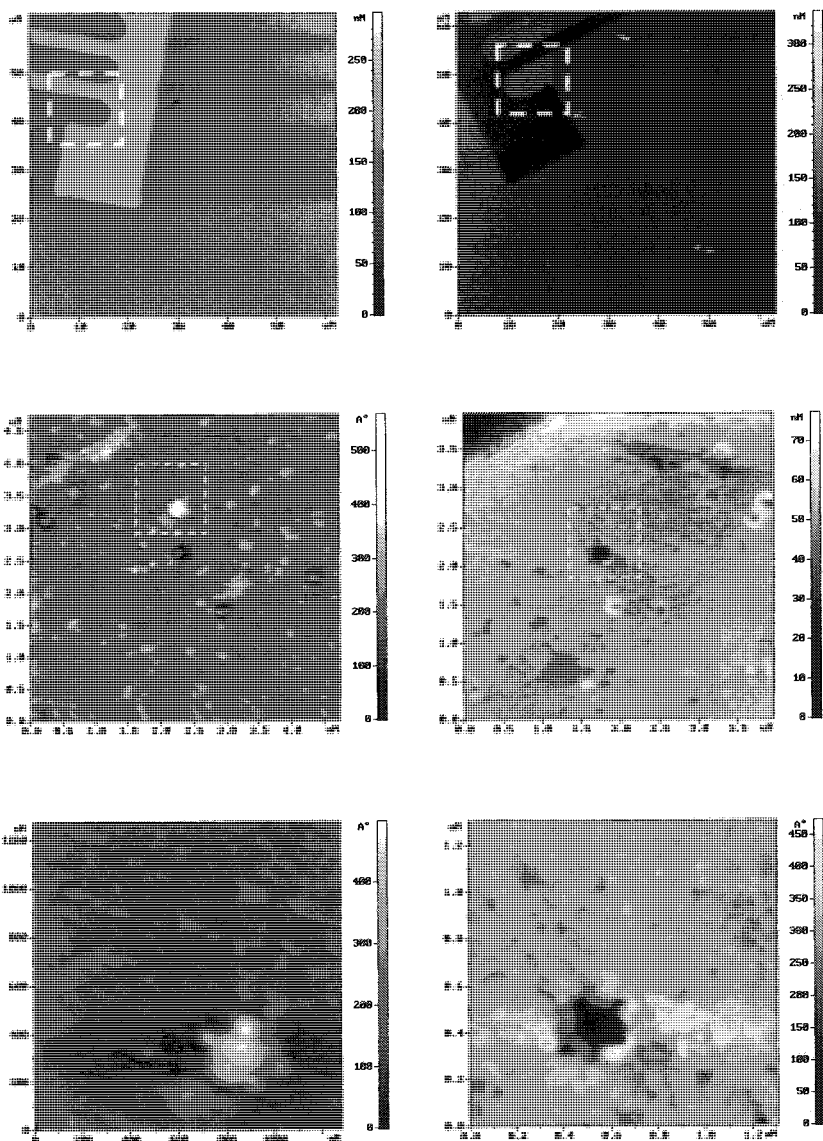


Figure 2. AFM investigations of conjugated areas of etalon surface (left) and polymer replica surface (right). The square on AFM images indicates the spot of successive scan runs.

Multilayer Mo-Si X-ray mirrors (MXM) for 13 nm wavelength have been prepared on combined glass-polymer substrates by magnetron sputtering [5]. For comparison, similar MXM structures have been formed at the same conditions on etalon Si substrates. As shown by XRR (Fig. 3), the FWHM and peak values of the reflectivity spectral curve for MXM grown on combined substrates practically coincide with similar characteristics for the mirrors on Si substrates. The experimentally observed decrease in reflectivity by 1–2% as compared to Si-based MXM can be attributed to further development of the polymer surface relief under the action of the high-energy component of the magnetron beam in formation of the first MXM layers.

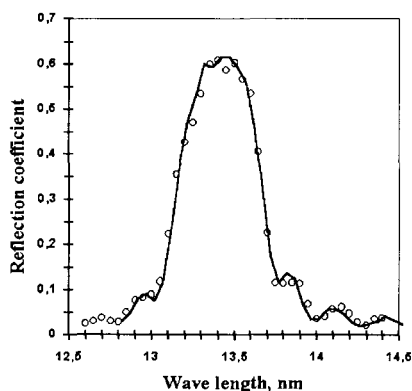


Figure 3. Spectral dependences of reflectivity for Mo-Si MXM formed on combined polymer-glass (circles) and etalon Si (solid line) substrates.

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SELF-ORGANIZATION PHENOMENA IN PULSED LASER ANNEALED Si/Ge SUPERLATTICES

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Si₅Ge₅ superlattices (SL) were treated by 80 ns pulses of a ruby laser in a wide range of energy densities. The induced structural and electronic changes were monitored *in situ* by time resolved reflectivity (TRR) and *ex situ* by scanning electron microscopy (SEM), Raman scattering and atomic force microscopy (AFM). The SL starts to melt at energy densities typical for bulk Ge (less than 0.4 J/cm²). At ≥ 0.7 J/cm², a self-organization phenomenon is observed. A system of quasiregular rectangular grains with linear dimensions of about 100 nm is developed on the sample surface.

1 Introduction and experimental

The melting of materials due to short laser pulses is an extremely nonequilibrium phenomenon. In a heterogeneous system, such processes as intermixing, interdiffusion and segregation are added. This makes the situation quite unpredictable and lets expect novel phenomena.

A Si₅Ge₅ superlattice (the lower indices designate the number of atomic monolayers in a SL period) containing 360 periods with an entire thickness of ~500 nm was grown by MBE at 500°C on a (001) Si substrate on top of a thin (50 nm) relaxed Si_{0.4}Ge_{0.6} buffer. The layer sequence terminated with a 10 nm thick Si cap. The wafer was irradiated by single 80 ns pulses of a ruby laser upon normal incidence. The experimental setup for the time resolved reflectivity (TRR)

measurements was described in detail elsewhere [1]. The Raman spectra were measured at RT with a micro-Raman setup (Jobin Yvon Spex T 64000). SEM was performed by a Hitachi S-4100 microscope and AFM images were obtained with a Digital Instruments AFM Nanoscope IIIa apparatus.

2 Results and discussion

The Raman spectrum taken prior to laser irradiation reveals features typical of a Si_mGe_n SL [2,3] (Fig. 1).

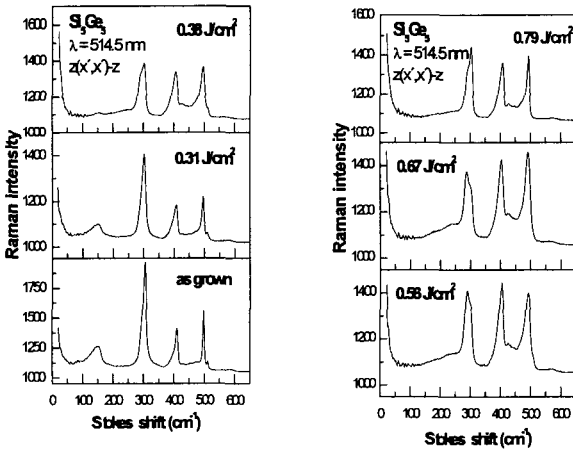


Figure 1. Raman spectra of the Si_3Ge_3 superlattice, as grown and laser annealed with the energy densities indicated. The peaks at 499, 410 and 305 cm^{-1} belong to the Si-Si, Si-Ge and Ge-Ge modes, respectively. The band at 150 cm^{-1} is due to the folded acoustical phonons (FAP). The first three modes also appear in the Raman spectra of a SiGe alloy, though at slightly different frequencies [4]. The FAP band is a fingerprint of the SL. A weak peak at 511 cm^{-1} is observed (Si-Si vibrations in the capping layer).

After the laser treatment with energy densities lower than 0.3 J/cm^2 , neither a visual change of the surface color nor changes of the surface morphology are observed. At 0.31–0.34 J/cm^2 , a transient change of the reflectivity is observed (Fig. 2). In the SEM, one observes some cracks (like those for 0.39 J/cm^2 , Fig. 3, but less pronounced). In the Raman spectrum, the FAP peak gets weaker relatively to the other bands and the Si-Ge mode grows as compared to the Si-Si and the Ge-Ge peaks. Three weak features appear at the low-energy side of the Si-Si peak, which were previously attributed to localized Si-Si optical modes whose frequencies are lowered because of the larger mass of neighboring Ge atoms [3]. At 0.37–0.39 J/cm^2 , the changes of the TRR become stronger and its behavior gets nonmonotonous. This behavior is then observed till 0.67 J/cm^2 (Fig. 2.) More pronounced cracks are observed in SEM. The FAP is strongly reduced in the Raman spectrum. In the range of 0.46 - 0.64 J/cm^2 the FAP peak almost entirely disappears. However the Si-Si peak from the capping layer still can be observed. At 0.67 J/cm^2 , the SL Si-Si Raman peak increases again and the Si-Si peak caused by the cap disappears. At 0.71 J/cm^2 , the TRR behavior gets much simpler than at lower energy densities. The most surprising change occurs in the surface morphology as observed by SEM: a system of quasi-regular rectangular “cells” with linear

dimensions of about 100 nm emerges (Fig. 3). A preliminary AFM study shows that the elementary building blocks of this new structure are rather crystallites or grains than concave cells (Fig. 4).

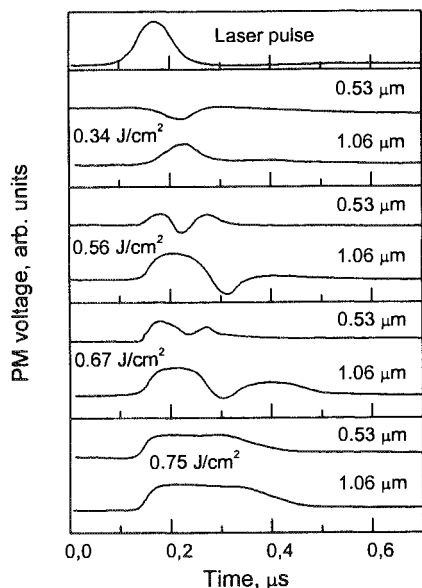
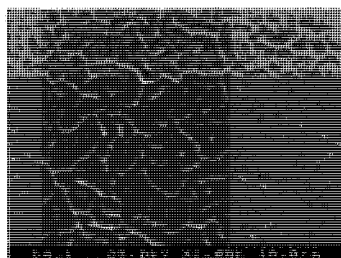
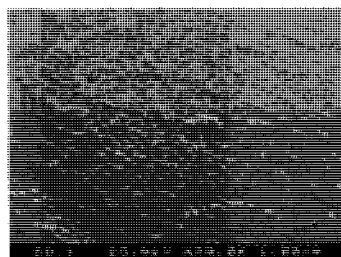


Figure 2. Time resolved reflectivity at two wavelengths (1064 nm and 532 nm) of the Si_3Ge_3 superlattice during pulsed laser annealing with the energy densities indicated.



a) 0.39 J/cm^2



b) 0.79 J/cm^2

Figure 3. SEM images of the surface of the Si_3Ge_3 superlattice subjected to pulsed laser annealing with the energy densities 0.39 J/cm^2 and 0.79 J/cm^2 .

We propose the following explanation of the observed behavior. In the range of 0.31 - 0.37 J/cm^2 , melting of the SL starts in the Ge layers because Ge has a lower melting temperature than Si (1211 K and 1687 K, respectively [5]). Nevertheless, due to the very small thickness of the Ge and Si layers in the SL, they probably melt almost simultaneously. Thus, the melting and subsequent intermixing of a part of the SL situated close to the surface (and thus contributing most strongly to the Raman spectrum) causes a diminution of the FAP band intensity and a growth of the Si-Ge mode intensity in the Raman spectra. However, the much thicker (10 nm) Si cap layer does not melt below an energy density of 0.7 J/cm^2 , although we believe that there is some dissolution of the capping layer in the molten SiGe alloy.

Below 0.7 J/cm^2 , the Si cap suffers strong deformations caused by the melting of the subjacent layer, which is manifested by the cracks seen by SEM and disordered seen in AFM. The recrystallization at these relatively low energy densities starts from both interfaces Si cap/melt and melt/solid SL (or buffer or substrate), so that the existence of a solid surface layer with the thickness varying

over the time causes interferences of the probing beams and thus the complicated behavior of the TRR observed in the experiment.

When the Si cap melts at 0.7 J/cm^2 , it experiences an intermixing but the surface layer remains enriched by Si after solidification, as evidenced by the vanishing of the weak Si-Si peak at 511 cm^{-1} and by the growth of the intensity of the main Si-Si peak. The interference phenomena in the TRR curves disappear because of the disappearance of a solid layer on top of the structure.

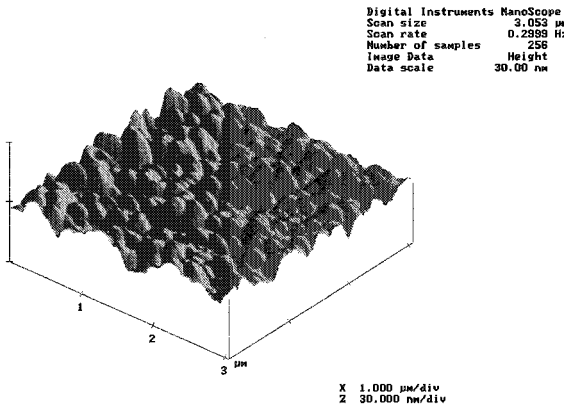


Figure 4. SEM images of the surface of the Si_5Ge_3 superlattice subjected to pulsed laser annealing with the energy density 0.79 J/cm^2 .

An intriguing question is that of the driving force causing the formation of the “cells” or nanocrystallites observed in SEM and AFM. It is well known that segregation of components occurs in the course of laser melting and solidification of Si-Ge alloys [6], with segregation effects quite dramatic in some case. Another origin of the self-organization may be strain caused by the discrepancy of the lattice constant of the Si substrate and the solidifying Si-Ge alloy. Further experiments, which show a variety of other details proving the self-organized character of the observed phenomena, are underway.

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AFM INVESTIGATION OF HIGHLY ORDERED NANORELIEF FORMATION BY ANODIC TREATMENT OF ALUMINUM SURFACE

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AFM investigation of aluminum surface after anodic treatment was performed. It was shown that electropolishing in HClO_4 based solutions and long-time anodic oxidation result in formation of highly ordered nanorelief on the aluminum surface. Applications of such treatments in nano- and optoelectronics are discussed.

1 Introduction

Porous anodic alumina (PAA) films attracts an interest because of possibility of low-cost and short time production of highly ordered nanostructures. Possibility of magnetic [1], semiconducting [2] and photonic [3] nanostructure formation on the basis of PAA was demonstrated last decade. It is known that highly ordered PAA films may be formed on pretextured aluminum surface [4]. There are the two commonly used techniques of ordered nanorelief formation: by electropolishing in perchloric acid ethanolic solution [5] or by two-step anodization [6].

In this paper, we present AFM investigation of the above mentioned processes. An application of PAA for fabrication of magnetic nanocrystals and carbon nanotubes is demonstrated. A possibility of terabit memory production with PAA templates and nanomasks is analyzed.

2 Sample preparation

Two types of aluminum were used as a substrate for highly ordered nanostructure formation. (1) Al (99,99%) foil is used for electropolishing and two-step anodization experiments; (2) vacuum deposited Al film of 10 μm thickness is used

for the two-step anodization only. Electropolishing was performed in the solution (vol.%) $\text{HClO}_4\text{:C}_2\text{H}_5\text{OH:H}_2\text{O}=6\text{:}80\text{:}14$ at a constant potential 10-70 V during 20-60 s. The two-step anodisation was performed in 40 g/l oxalic acid aqueous solution at 10 mA/cm^2 current density. After both steps of processing the alumina film was etched in CrO_3 and H_3PO_4 mixture at 90 $^\circ\text{C}$.

AFM investigation of aluminum surface was performed by scanning probe microscope "Solver P47H" (NT-MDT Co., Russia) in the non-contact mode.

3 Results and discussion

AFM images of Al surface after electropolishing and anodic oxidation are presented in Fig. 1. The best results of electropolishing is obtained at 60 V etching potential for 30 s. As the result of this process 50 μm of Al was dissolved. The period of the nanopattern was about 80 nm independently on electrolyte concentration. Maximum height of the pattern was 4-6 nm.

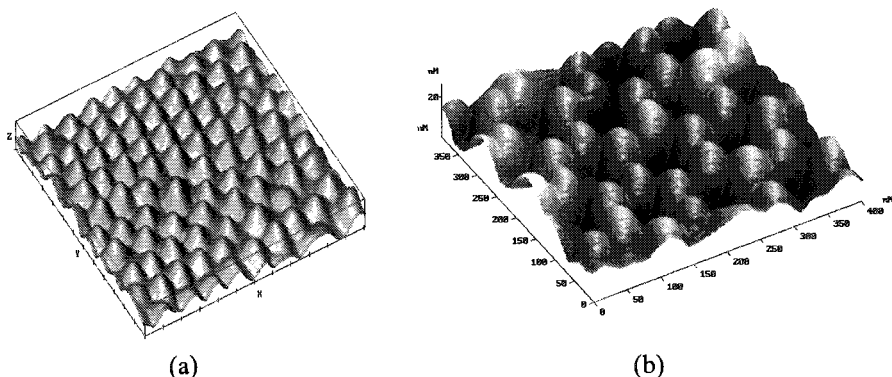


Figure 1. AFM images of Al surface produced by electropolishing (a) and anodic oxidation (b) recorded after removal of the oxide.

Long-time anodization of Al in the oxalic acid solution produces the nanorelief with 50 nm period and 20 nm height. An acceptable ordering was achieved during 1 h oxidation when 9 μm of Al was converted into oxide.

Comparison of the above mentioned techniques shows that long-time oxidation allows to form high contrast nanostructures with the lower Al consumption. Therefore, the second technique is more suitable for the formation of ordered nanostructures not only at a foil surface, but also at evaporated Al films.

Further anodization of the pretreated surfaces showed that the ordering degree is much higher at the long-time anodized surface. By our opinion this results from the large height of a nanorelief.

Additionally, we investigated features of nanoimprinted Al surface anodization. Nanoimprinting was performed by indentation of surface with the AFM tip.

Pyramidal pits of 20 nm were formed at the surface of annealed Al. This technique allowed us to form an individual carbon nanotube (CNT) in PAA template. CNT deposition was performed by commonly used PECVD process. Also, we formed the arrays of vertically aligned CNT in PAA with cathodically deposited and evaporated metal catalyst.

The ordered PAA back-side and structured Al surface were used to produce self-organized metal nanoparticles. We used Au or amorphous carbon as add-layer for deposition of Ti or Fe nanostructures. Both these metals have a weak wetting of the add-layer. The deposition was performed by a laser induced plasma deposition technique. In this process the energy of ions was about 20 eV. The highly ordered curved substrate surface defined position of the deposited clusters providing formation of highly ordered arrays of metal nanoclusters. A perspective application of such structures for terabit memory was demonstrated. For example, Ti nanoclusters covered by native oxide demonstrated irreversible transformation of I-V characteristics from barrier-like to the ohmic behavior after the action of current supplied by a tip of conductive AFM.

Thus, the results obtained show the possibility to apply Al for fabrication of large-area highly-ordered nanostructures.

Acknowledgements

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QUASI-1D CHANNELS IN Si DELTA-DOPED GaAs GROWN ON VICINAL (111)A GaAs SUBSTRATES

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A novel delta-doped by Si GaAs epitaxial structures were grown by a MBE method on vicinal (111)A substrates with misorientation angles of 0.5° , 1.5° and 3° respect to the $[2\bar{1}\bar{1}]$ direction. It was found that the resistivity of structures R_{pa} along the steps of vicinal surface is lower than that of R_{pe} across the steps and depends on temperature. The anisotropy of resistance is explained by quasi-1D channels or at least 1D periodic modulation of the 2D electrons in the structure. All samples showed p-type conductivity.

1 Introduction

The epitaxial structures with quasi-1D and 1D conducting wires are widely studied during last years. The perspective method for obtaining such structures is the growth of the structures by molecular-beam epitaxy (MBE) on the vicinal GaAs surface with δ -layers of Si or Sn [1-3]. Due to high diffusive mobility, Si or Sn is segregated and is accumulated predominantly at the edges of terraces. In the present work, δ -Si doped GaAs epitaxial structures grown by MBE on vicinal (111)A substrates with different misorientation angles were investigated.

2 Samples

In contrast to GaAs with orientation (100) where silicon predominantly behaves as a donor it is possible to obtain both heavily compensated semi-insulating layers, and layers with n- or p-type of conductivity in epitaxial structures grown on (111)A GaAs substrates [4]. It depends on the growth temperature, ratio of arsenic to gallium flux Υ ($\Upsilon = P_{As}/P_{Ga}$, where P_{As} and P_{Ga} are the partial pressures of As and Ga) [5,6]. It is known [5], that at a misorientation of (111)A GaAs substrate respect to the $[2\bar{1}\bar{1}]$ direction on small angles α the vicinal surface shows the terraces with orientation (111)A and steps with orientation (100). In Fig. 1a the

arrangement of Ga and As atoms on such vicinal surface is shown. If a Si δ -layer is grown on such surface, it is expected that Si behaves as a donor on steps (with orientation (100)). The behavior of Si on the terraces (having orientation (111)A) may differ and depends on conditions of the growth. As a result a formation of 1D hole channels on the terraces of the vicinal surface is expected.

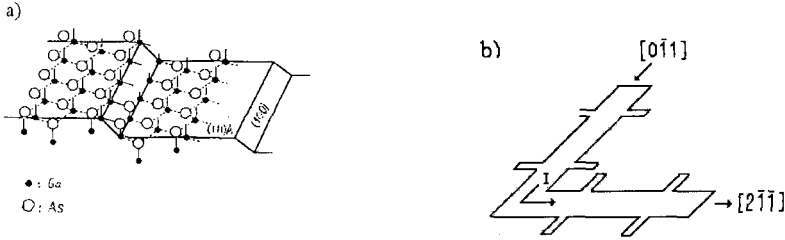


Figure 1. Schematic arrangement of Ga and As atoms on a (111)A surface with a misorientation of the substrate respect to the $[2\bar{1}\bar{1}]$ direction (a), and schematic view of the Hall bridge for measurements of resistance anisotropy (b).

The samples were grown by MBE on semi-insulating (111)A GaAs substrates, inclined from a (111)A plane toward a $[2\bar{1}\bar{1}]$ direction with angles of $\alpha = 0.5^\circ, 1.5^\circ$ and 3° . All these samples, and also reference sample with orientation (100), were grown simultaneously. The relevant parameters of the structures are listed in Table 1. The grown structures included an undoped GaAs buffer layer of $0.42\ \mu\text{m}$ thickness, δ -Si doped layer, undoped GaAs layer of $50\ \text{nm}$ thickness and uniformly doped GaAs cap layer of $30\ \text{nm}$ thickness with silicon concentration about $10^{18}\ \text{cm}^{-3}$ in order to suppress the surface depletion. The epitaxial growth was carried out at 610°C with Υ equals to 14. After the growth, the samples were prepared for galvanomagnetic measurements as L-shape Hall bridges by a photolithography method (Fig. 1b).

The resistance of structures was measured by a four-contact method simultaneously parallel and perpendicularly to the step edges of vicinal surface in the temperature interval $4.2\text{--}300\ \text{K}$. The Hall effect and magnetoresistance were investigated in magnetic fields up to $0.5\ \text{T}$.

3 Anisotropy of resistance

All vicinal samples possessed p-type conductivity with mobility $\mu \approx 80\ \text{cm}^2/\text{Vs}$ at $77\ \text{K}$. An anisotropy of resistance along (R_{pa}) and crosswise to steps (R_{pe}) has been observed. The temperature dependence of resistance for samples S2 and S3 in a direction $[0\bar{1}1]$ (pa-direction) and in $[2\bar{1}\bar{1}]$ (pe-direction), and also an anisotropy of resistance $k_{\text{an}} = R_{\text{pe}}/R_{\text{pa}}$ are shown in Fig. 2.

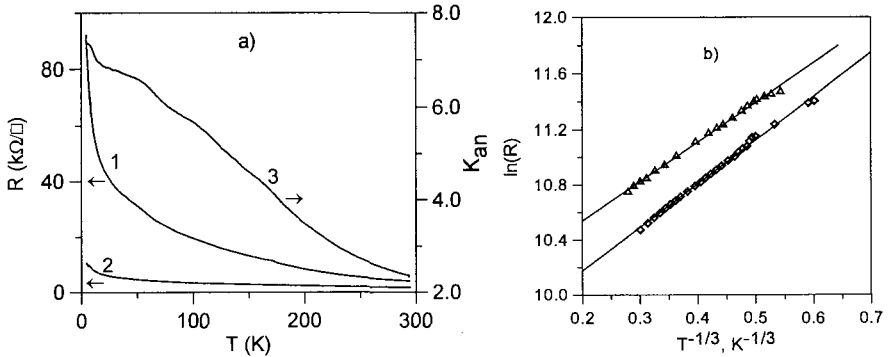


Figure 2. Temperature dependence of resistances for sample S2 in $[2\bar{1}\bar{1}]$ (1, R_{pe}) and $[0\bar{1}1]$ (2, R_{pa}) directions, and the anisotropy of resistance $k_{an} = R_{pe}/R_{pa}$ (3) (a). Logarithm of resistance along a $[2\bar{1}\bar{1}]$ direction as a function of $T^{-1/3}$ for samples S2 (squares) and S3 (triangles) (b).

For all vicinal samples a resistance R_{pe} perpendicular to the step edges are higher than resistance R_{pa} parallel to the steps. The anisotropy of resistance k_{an} is increased under cooling. The same dependence of k_{an} was observed earlier in vicinal GaAs structures with δ -doping by tin [4]. The anisotropy of resistance decreased when the angle of misorientation increased from $\alpha=0.50$ to $\alpha=3.00$. A reference sample S1 had an n-type conductivity and $\mu \approx 2000 \text{ cm}^2/\text{Vs}$. The anisotropy of resistance in this sample was not found. Some parameters for all samples at two temperatures are listed in Table 1.

Table 1. Sheet resistance R_{pa} parallel to the step edges, anisotropy of resistance R_{pe}/R_{pa} and Hall density of holes p_H or electrons n_H at 300 K and 77 K for vicinal (111)A samples with different misorientation angles α and for the reference (100) sample.

Sample	300 K			77 K		
	R_{pa} ($k\Omega/\square$)	R_{pe}/R_{pa}	n_H, p_H (10^{12} cm^{-2})	R_{pa} ($k\Omega/\square$)	R_{pe}/R_{pa}	n_H, p_H (10^{12} cm^{-2})
S1, (100)	0.305	1.0	$n_H=12$	0.28	1.0	$n_H=11.6$
S2, $\alpha=0.5^\circ$	1.75	2.3	$p_H=28$	3.91	6.0	$p_H=3.3$
S3, $\alpha=1.5^\circ$	2.60	1.1	$p_H=21$	23.1	1.5	$p_H=3.6$
S4, $\alpha=3.0^\circ$	3.54	1.0	$p_H=21$	23.7	1.0	$p_H=3.6$

The anisotropy of resistance is most likely due to the different behavior of silicon on steps and terraces of vicinal surface. Si atoms on terraces under the growth conditions are donors, while on steps they are acceptors. Electrons at steps compensate the nearest holes at terraces. Thus, quasi-1D channels of p-type are formed along vicinal steps and the anisotropy of conductivity occurs.

The density of holes drops rapidly when temperature decreases from room down to nitrogen temperature (Table 1), and at helium temperature the Hall effect is not measurable.

4 Hopping conductivity

At low temperatures ($T < 50$ K) resistance obeys to the Mott law for variable range hopping conductivity in 2D case $\rho = \rho_0 \exp\{(T_0/T)^{1/3}\}$ (Fig. 2b). For samples S2 and S3 parameters T_0 is equal to 31 K and 23 K respectively for current directed perpendicular to steps, and 22 K and 18 K for a current directed along the steps. Parameter T_0 is connected to density of states at the Fermi level and radius of localization $T_0 = C(N_{E_F} a^2)^{-1}$, where $C=13.8$, N_{E_F} is density of states at the Fermi level. Radius of localization a calculated for sample S2 is approximately 60 nm for current along steps and 72 nm for current perpendicular to the steps.

5 Conclusion

At selected modes of epitaxial growth silicon on vicinal (111)A surface is an acceptor and gives an anisotropy of resistance due to formation of quasi-1D channels in the $[0\bar{1}1]$ direction.

Acknowledgements

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NUCLEATION OF SUPERCONDUCTING PHASE IN MULTILAYERED NANOSTRUCTURES

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An influence of finite dimensions of multilayered nanostructures on superconducting phase nucleation and vortex mobility is studied both experimentally and theoretically. Resistive characteristics are observed to be sensitive to the geometrical symmetry of samples. For multilayers with the symmetry plane in the superconducting layer the resistive transitions are widely spread with respect to the samples with the symmetry plane in normal layers. This result is explained by the joint action of Lorentz and pinning forces on the nascent vortex lattice.

1 Introduction

Investigations of superconducting multilayered nanostructures (SMN) can be carried out on one side by analyzing the superconducting state close to the upper critical perpendicular $H_{c2\perp}(T)$ and parallel $H_{c2\parallel}(T)$ magnetic fields [1,2], and, on the other side, by analyzing the current capability of SMN at different magnetic fields H and temperatures T . The latter gives information about pinning mechanisms of vortex medium in the presence of anisotropy, which is still an open matter [3]. The background for the microscopic theoretical investigation of SMN in the vicinity of H_{c2} has been given in the classical work of Takahashi and Tachiki (TT) [2]. However, difficulties arise when trying to fit experimental dependencies for both $H_{c2\perp}(T)$ and $H_{c2\parallel}(T)$ [4]. They can be resumed as follow: only the simplest cases of the TT-theory can be applied to obtain successful experimental data fitting, but this limit can be overcome by simple phenomenological extension of the theory; the TT-theory has been created for the case of an infinite superlattices, but, as we are going to demonstrate, the finiteness of the sample is a crucial point that cannot be neglected. In this contribution we present results related to this last observation. We investigate the stability of the nascent vortex lattice in samples with different symmetries and its influence on the resistive characteristics of SMN.

2 Experimental results

Multilayers of Nb (superconducting) and Cu (normal metal) with different number of bilayers N_{bil} were grown on Si (100) substrates at room temperature by using a dual source magnetically enhanced dc triode sputtering system. The specimens were characterized by resistive transition temperature measurements both at perpendicular and parallel orientations of the external magnetic field. All the Nb/Cu multilayers have identical copper and niobium thickness, 200Å. The first and the last layers are always made of Cu. It means that for the samples with odd number of bilayers the plane symmetry falls into the center of superconducting (S) layer, while for the samples with even number of bilayers it falls in the center of normal (N) layer. Taking into account practically the same superconducting properties of all the samples, we may assume the identical properties of interfaces. The only remain difference is the total number of bilayers, i.e. the geometrical symmetry.

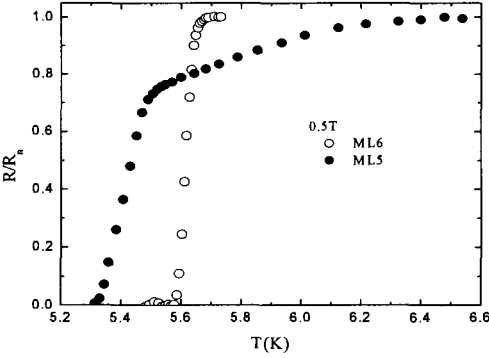


Figure 1. Resistive characteristics for sample ML5 (closed circles) and ML6 (open circles) at parallel magnetic field of 0.5 T.

In Fig. 1 we show typical $R(T)$ behavior in parallel orientation of the magnetic field of 0.5 T for two samples, ML5 with $N_{bil}=5$ (S type) and ML6 with $N_{bil}=6$ (N type). The resistive characteristics are quite different and depend on the type of the samples symmetry. For the N-type sample (ML6) the usual sharp curve reveals the resistive fall down to zero. For the S-type sample (ML5) the superconductor transition is broadened. At large magnetic fields $R(T)$ curves become sharp for both the samples. The behavior shown in Fig. 1 has been found for all our samples with S- or N- type symmetry.

3 Model and discussion

3.1 Nucleation of superconductivity in SMN

We consider a coordinate system with the XY plane parallel to the layer surface, coinciding with the symmetry plane of the S/N structure, and the Z-axis perpendicular to the layer surfaces. In the vicinity of $H_{c2||}$ the Ginzburg-Landau

(GL) wave function $\Psi(\mathbf{r})$ becomes negligibly small, and for the vector potential $\mathbf{A}(\mathbf{r})$ in the first approximation one can get $\mathbf{A}(\mathbf{r}) = (H_0 z, 0, 0)$, where H_0 is the external magnetic field. By separating the variables for the wave function in the XZ plane, $\Psi(\mathbf{r}) = e^{ikx} \cdot \psi(z)$, we may write the following equation for $\psi(z)$ [5]

$$\left(\partial_z^2 + \eta(z) - H_0^2 \cdot (z - z_0)^2\right)\psi(z) = 0, \quad (1)$$

where we have defined $z_0 \equiv k/H_0$ and η is the step function [6]. The boundary conditions for the wave function $\psi(z)$ are the following

$$\frac{\partial \psi}{\partial z}(L/2) = \frac{\partial \psi}{\partial z}(-L/2) = 0, \quad (2)$$

where L is the multilayer overall thickness. At each S/N interface equation (1) is accompanied by the condition [3]

$$\frac{1}{\psi_S} \frac{\partial \psi_S}{\partial z} \Big|_{\Gamma_i} = P \frac{1}{\psi_N} \frac{\partial \psi_N}{\partial z} \Big|_{\Gamma_i}, \quad (3)$$

where $i=1,2,\dots,l-1$, l is the total number of layers in SMN, P is the boundary transparent coefficient and $\psi_{S(N)}$ is the wave function in the S(N) layer. The boundary conditions (2) and (3) at fixed temperature and for each value of z_0 determine the task of eigenvalues $H_0 = H_0(z_0)$ for equation (1). The parameter z_0 is determined by minimizing of the GL functional, which means, together with the boundary conditions for the field $H(\mathbf{r})|_{z=\pm L/2} = H_0$, a test for the function $H_0(z_0)$ extremum. The maximum eigenvalue of H_0 is the upper critical field $H_{c2||}$.

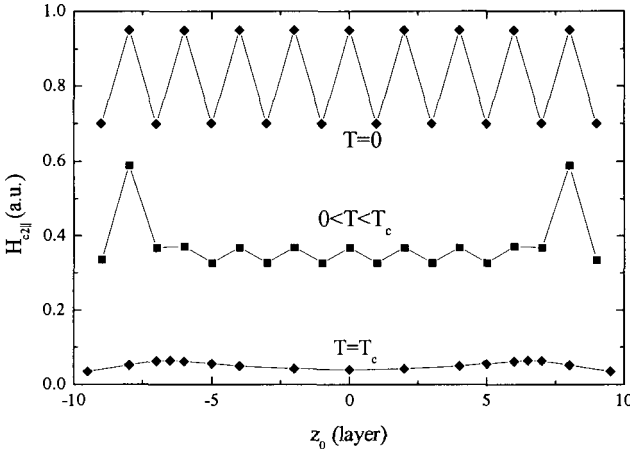


Figure 2. The $H_{c2||}$ versus z_0 dependence at different temperatures for SMN.

Simultaneously we can obtain the position of the superconducting phase nucleus. Numerical calculation of $H_0(z_0)$ dependence (Fig. 2) reveals its oscillating character in the overall temperature range except the region close to T_c . The local maxima of the function $H_0(z_0)$ belong to the centers of the S layers, while local minima fall in the centers of the N layers. For $0 < T < T_c$ the superconducting phase

nucleus is formed in the outer superconducting layer. At sufficiently low temperatures the difference between local maxima of $H_0(z_0)$ becomes negligible and the maximum eigenvalue is in a state of degeneracy N_{bil} . For $T \approx T_c$ the GL wave function is delocalized over the whole sample, this corresponds to the classical interpretation of dimensional crossover for SMN.

3.2 Symmetry and resistive characteristics

The studied SMN's are hard type II superconductors. So, the vortex lattice is formed while H_0 becomes slightly less than $H_{c2||}(T)$. We will focus on the dependence of the vortex lattice nascent process on the $R(T)$ curves. At low temperatures, when the degeneracy of H_0 is N_{bil} , a rather stable vortex lattice is formed. The perturbation of the lattice due to feeble bias current is smaller with respect to the interface pinning force. The $R(T)$ curve is sharp both for S- and N-type samples. This scenario is relatively trivial.

The physical picture becomes more complicated when the temperature increases towards the critical value T_c . As shown in Fig. 2, a double degeneracy of H_0 occurs. at some temperatures. In order to construct the wave function in the first order perturbation theory, the ground state wave function must be written as

$$\Psi^{(0)}(\mathbf{r}) = c_1 e^{ikx} \cdot \psi(z) + c_2 e^{-ikx} \cdot \psi(-z). \quad (4)$$

One of the results of the first order perturbation theory calculations is the equality $c_1 = c_2$. This corresponds to the formation of the vortex chain in the plane symmetry XOY of the SMN. This one-dimensional vortex lattice is not stable with respect to external forces as a usual two-dimensional lattice. The bias current creates Lorentz force, which acts on the vortex lattice. Moreover, vortices are situated in the field of the pinning force created by the periodical structure of the SMN.

The joint action of pinning and Lorentz forces on vortex chain depends on the geometrical symmetry of the nanostructure. For the SMN of N-type the vortex chain is located in the center of N layer and the pinning force obstructs the vortex penetration inside the S layer. As bias current flows through the superconducting parts of the sample, dissipative processes are absent and the resistive transition is sharp (Fig. 1). For S-type nanostructures, vortex chain nucleates inside the central superconducting layer. Electromagnetic interaction between vortices and bias current leads to dissipation, it follows that in the central layer the sample resistance is not suppressed completely and the resistive transition becomes wider.

4 Conclusion

We have analyzed a possible influence of the vortex lattice nascent process on the resistive characteristics of superconducting multilayered nanostructures with different geometrical symmetry. In order to achieve the temperature dependences of both the parallel and the perpendicular critical magnetic fields, we have considered

joint action of Lorentz and pinning forces on vortex lattice in SMN. Moreover, a new concept of dimensional crossover follows from our study. For low temperatures we indeed get the two-dimensional state. Close to T_c the superconducting phase does not follow the classical three-dimensional scenario. In this temperature range, we found that the influence of surface superconductivity becomes more important and must be taken into account.

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CERAMIC FILTER MATERIALS WITH GRADED MICRO/NANOPOROUS STRUCTURE FABRICATED BY LASER SINTERING

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Laser sintering of ceramic fine powders deposited onto ceramic substrates is shown to be an appropriate technique to fabricate micro- and nanoporous ceramic filters. The requirements to the filter materials are discussed.

1 Introduction

Lasers open wide opportunities in nanotechnologies. Today lasers are used for the synthesis of fullerenes and nanotubes as well as nanoparticles of different matters. They are also used in the fabrication of nanofilms and nanowires. One of the important applications of lasers can be connected with the assembling of nanocomponents. In particular, it is promising to perform welding of nanowires by focused laser beams. Besides, lasers can be applied to best advantage in the nanopowder technologies. In this paper we consider possibilities to produce nanoporous filter materials using laser sintering technique.

2 Technical approach and its justification

The membrane nanoporous layers are proposed to be formed by laser sintering of nanopowders deposited onto the surface of microporous structure by sol-gel sedimentation/centrifugation technique. In principle, the method of laser sintering is well known [1]. However, there is no wide application in practice of nanopowder processing up to date. A number of constraints defines what quality of sintered structure may or may not be achieved by this technique. On the whole, the comprehension of nanopowder sintering mechanisms by laser radiation is rather low.

It is supposed that due to the short time of laser sintering undesirable recrystallisation processes are prevented or limited. Besides, optimum conditions for formation of nanoporous layer during laser sintering are provided due to specific ability of nanoparticles to consolidation. As a result, the filter materials possess increased filtration fineness and throughput in comparison with the analogical

materials produced by conventional techniques, while the strength can be comparable.

3 Experimental investigations

Experiments were started with the metal powder in order to reveal principal possibilities of laser sintering of powder layers deposited onto a substrate [2]. In these experiments, the layer of Ni powder (with particle size about $0.5\text{ }\mu\text{m}$) was deposited onto the surface of Ni substrate manufactured by traditional powder metallurgy (with particle size about $5\text{ }\mu\text{m}$) and subjected to sintering by CW-Nd:YAG laser ($\lambda = 1.06\text{ }\mu\text{m}$). Layer thickness was about $2\text{ }\mu\text{m}$. The joining of powder layer with the substrate was provided during sintering. The graded porous structure was formed on the surface as it is shown in Fig. 1 (the size of pores is about $2\text{ }\mu\text{m}$ for the sintered layer and $6\text{ }\mu\text{m}$ for the substrate).

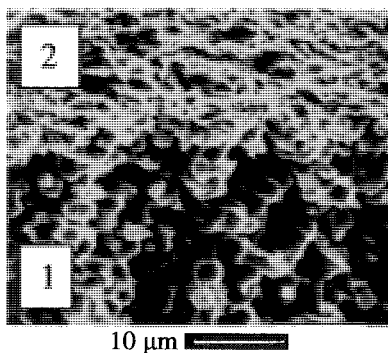


Figure 1. Graded structure on the surface of substrate (fracture of Ni substrate (1) with sintered Ni powder layer (2) on the surface; top view). $Q = 50\text{ W/cm}^2$; $t = 60\text{ s}$; vacuum.

In these experiments, the positive effect of sintering was achieved first of all due to high heat conductivity of metal powders. On the contrary, ceramic powders have low heat conductivity. Therefore, it was rather difficult to sinter these powders when they were similar to metal ones in particle size (about $0.5\text{ }\mu\text{m}$). To overcome the problem ceramic powders with smaller particles were used. As it is known, the fine powders are susceptible to sintering due to greatly reduced melting point.

The Al_2O_3 powder (with the particle size up to $0.25\text{ }\mu\text{m}$) was used in the study. It was deposited onto the surface of Al_2O_3 substrate manufactured by traditional ceramic technology (with the particle size about $3\text{ }\mu\text{m}$) and subjected to sintering by CW- CO_2 laser. For this type of laser radiation, there is a maximum of the light absorption by the powder [3]. For different experiments the layer thickness was varied and achieved $30\text{ }\mu\text{m}$. Joining of powder layer with the substrate was provided during sintering. As a result, the graded porous structure was formed on the surface as it is shown in Fig. 2 (the size of pores is less than $1\text{ }\mu\text{m}$ for the sintered layer and up to $3\text{ }\mu\text{m}$ for the substrate).

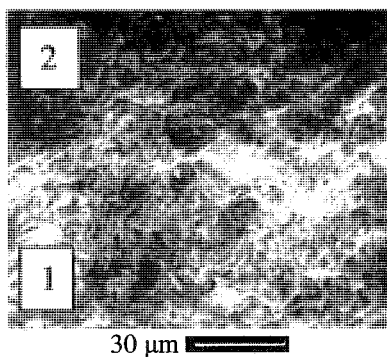


Figure 2. Graded structure on the surface of substrate (fracture of Al_2O_3 substrate (1) with sintered Al_2O_3 powder layer (2) on the surface). $Q = 60 \text{ W/cm}^2$; $t = 10 \text{ s}$; air.

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NANOSTRUCTURE BASED DEVICES

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InGaN/GaN QUANTUM WELLS: FABRICATION, OPTICAL PROPERTIES AND APPLICATION IN LIGHT EMITTING DEVICES

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Main achievements in GaN-based light emitting devices have been analysed. Laser and optical properties of InGaN/GaN multiple quantum well heterostructures grown in AIXTRON MOVPE reactors were investigated as a function of temperature ($T = 80 - 450$ K) and excitation intensity ($I_{\text{exc}} = 0.01 - 1000$ kW/cm²) of the N₂ and HeCd laser radiation. Laser action was achieved in all types of the MQWs from the violet up to blue spectral region ($\lambda_{\text{las}} = 405 - 470$ nm). The laser threshold at room temperature was $35 - 100$ kW/cm² and $70 - 150$ kW/cm² for the “violet” and “blue” lasers, correspondingly. The maximal characteristic temperature was 530 K in the temperature range of 80 - 220 K for the “blue” lasers evidencing on the possible role of localised states in the gain mechanism. It was shown that the overheating of the active region under high excitation intensities can reach $\Delta T = 40 - 100$ K and is due to the inherent laser radiation.

1 Introduction

GaN-based compounds are very promising for light emitting devices such as light emitting diodes (LED) and laser diodes (LD) due to their wide interval of the band gap energies (ultraviolet - orange spectral region) and the chemical, thermal and mechanical stability [1-3]. The material system attracts much attention also for electronic applications due to its outstanding inherent electrical properties such as high breakdown voltages, high peak electron velocities and high sheet electron concentration especially in two-dimensional electron gas structures like high electron mobility transistors [4] and ultraviolet detectors [5] grown on sapphire and silicon carbide. AlInGaN-based LEDs have an output power of about 14 mW with a power density of about 300 kW/cm² at low operating voltage (3 V) and a current of 20 mA [1,2]. If the LED efficiency would be increased up to 50% and more, for example 200 lm/W, white light sources two times more efficient than fluorescent lamps and ten times more efficient than incandescent lamps can be produced. The world energy saving would be more than 1.000 TWh/year which is equal to approximately 100 atomic power stations.

An important place among these devices belongs to lasers. The violet lasers have lifetimes up to 15000 hours with a power of 30 mW [3]. The wavelengths of the LDs are shifted now from the violet up to blue spectral region [6].

However, especially for automotive and other applications in high-volume low-cost market segments, the choice of substrate is still an open question. Sapphire (Al_2O_3) suffers from a low thermal conductivity worsening the high-power operation of lasers, light emitting diodes and transistor devices. Silicon carbide is very expensive. Silicon is a promising alternative substrate for GaN growth because of its low cost, excellent quality, large-area availability and the possibility to integrate GaN-based light emitting devices and high power electronics with Si-based photodetectors and logical circuits. However, the main challenge connected with the use of silicon is the high mismatch in lattice constants and in thermal expansion coefficients [7].

Light emitting devices fabricated on Si show worse characteristics compared to devices grown on Al_2O_3 and SiC. The nature and reasons of the defects and electrical properties, the recombination mechanism and the influence of laser and thermal effects are not completely studied up to now. A comprehensive investigation of optical and electrical properties of GaN-based heterostructures grown on Si correlated to growth and processing technologies can lead to a better understanding the physical reasons of the existing problems. It can help also to establish any feedback with technology, to optimise it and to create the UV-visible light emitting diodes and lasers with characteristics comparable to that grown on Al_2O_3 and SiC.

During the last five years, we were engaged in the investigation of the growth and in the optical characterisation of different types of GaN epitaxial layers, InGaN/GaN single and multiple quantum wells (SQW, MQW) and electroluminescence test (ELT) heterostructures grown on sapphire substrates emitting in a wide interval of wavelengths from 390 nm to 530 nm. Most attention was paid to optimise the growth conditions, to create optically pumped lasers from UV up to the blue spectral region [8,9]. Optical pumping and optical methods of characterisation of these structures are the fastest ways to determine their properties and to optimize output characteristics of the optically pumped lasers. Lasing at $\lambda = 450 - 470$ nm was achieved for the first time [9]. In the course of the last year, new GaN layers and InGaN/GaN MQWs were grown on Si substrates. Laser action in UV [10] and blue [11] spectral regions was achieved in such structures for the first time.

In this paper, the author presents a short review of recent results achieved during the time period after "Nanomeeting-2001" on behalf of his colleagues from AIXTRON AG, Aachen, Germany (A. Alam, M. Luenenbuerger, H. Protzmann, B. Schineller, M. Heuken) where all samples were grown, from the Institute fuer Theoretische Elektrotechnik RWTH Aachen, Germany (Y. Dikme, H. Kalisch, A. Szymakowski) where layer growth and low temperature photoluminescence (PL) measurements were done and from the Institute of Physics of the National Academy of Sciences of Belarus, Minsk (A. L. Gurskii, E. V. Lutsenko, V. N. Pavlovskii, V. Z. Zubialevich) where laser and optical properties of all heterostructures under high excitation intensities were carried out. Most attention is paid to InGaN/GaN

MQWs grown on sapphire substrates. The optical and laser properties of the MQW heterostructures grown on silicon substrates are presented in additional paper for "Nanomeeting-2003".

2 Growth and measurements

All structures were grown in AIXTRON MOVPE reactors on 2-inch (0001)-oriented Al_2O_3 substrates at low pressures (200 mbar or 50 mbar), trimethylgallium (TMGa), trimethylaluminum (TMAI), trimethylindium (TMIn), ammonia (NH_3), Cp_2Mg and silane (SiH_4) were used as precursors. The deposition of a 30 nm low temperature GaN nucleation layer preceded the growth. After that, a 1.5 μm GaN buffer layer was grown at temperatures between 1050 - 1180°C using H_2 as a carrier gas. The stack of active layers including the InGaN quantum wells and GaN barriers was grown at 750 - 850°C using N_2 as a carrier gas. The thickness of the InGaN active layer was 3 - 5 nm, the thickness of the barriers was 4 - 6 nm and the thickness of the upper cap layer was 10 - 50 nm for the MQWs grown on sapphire (MQW/ Al_2O_3). The design of the ELT heterostructures grown on sapphire substrates (ELT/ Al_2O_3) was the following: GaN:Mg(250 nm)/5×(InGaN/GaN)/GaN:Si(1 μm)/GaN(1 μm)/nucleation layer / Al_2O_3 .

Photoluminescence (PL) and lasing were excited by the radiation of a N_2 laser ($h\nu = 3.68$ eV, $I_{\text{exc}} = 10^2 - 10^6$ W/cm², $f = 1000$ Hz, $\tau_p = 8$ ns), a HeCd laser ($h\nu = 3.81$ eV) and by radiation of a dye laser with frequency tuning for direct excitation of the quantum wells. The electroluminescence was excited by voltage imposed to the ELT samples by stripe contacts. Reactive ion beam etching (RIBE, $\text{Ar} + \text{O}_2$) was used for the formation of the contacts on the n-type region of the device and for removing of a part of the cap layer.

Fig. 1a shows the design of the GaN/ Al_2O_3 , InGaN MQW/ Al_2O_3 and InGaN MQW ELT heterostructures. An example of the ELT heterostructure laser and the geometry of excitation by the nitrogen and dye laser radiation are given in Fig. 1b.

3 InGaN/GaN multiple quantum well laser heterostructures

Laser action without any visible degradation was obtained in the InGaN/GaN MQW heterostructures up to $T = 585$ K. The laser spectra at low I_{exc} consist of one very narrow line with the lowest FWHM of 0.04 nm. All lasers had well pronounced threshold input-output characteristics. The external differential quantum efficiency of the laser operating at 452 nm for TE polarisation amounts to the value of $\eta = 3\%$. The maximum total energy and power per pulse from both facets were 300 nJ and 40 W, correspondingly, at room temperature for $\lambda_{\text{las}} = 452$ nm.

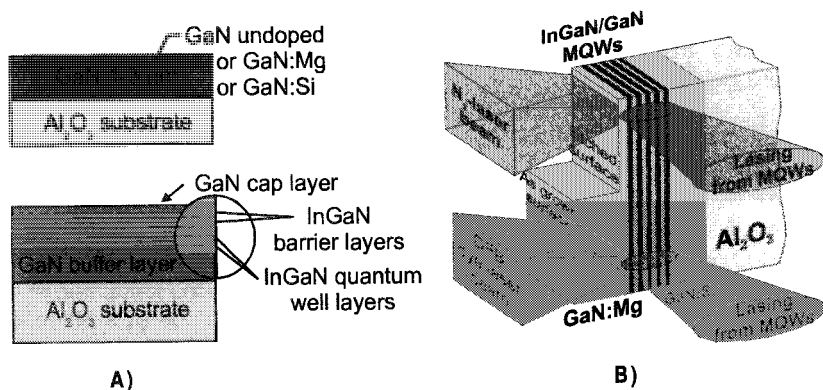


Figure 1. a) Layer design of GaN and InGaN/GaN multiple quantum wells grown on Al₂O₃ and on Si substrates. b) Scheme of InGaN ELT/Al₂O₃ heterostructure laser and geometry of excitation by nitrogen and dye laser radiation.

All investigated MQW structures had well-pronounced laser thresholds and clearly seen angular intensity distributions in the far-field pattern at excitation above the laser threshold. The far-field patterns of the laser emission consist of three or two light spots. The laser spectra were independent of the registration angle in the case of two light spots and were strongly dependent on the registration angle in the case of three light spots. The spatial distribution of the laser emission is formed by high-order transverse and leaky modes depending on the optical confinement factor.

Laser action was achieved in InGaN/GaN MQWs in the spectral range of 405 - 470 nm at room temperature. The laser threshold value depends on the operating wavelength. The laser threshold at room temperature reached the minimal value of $I_{\text{thr}} = 35 \text{ kW/cm}^2$ for the lasers operating at $\lambda_{\text{las}} = 430 \text{ nm}$ and the maximal value of about $100 - 130 \text{ kW/cm}^2$ for the lasers operating at wavelengths near the edges of the spectral range of 405 - 470 nm.

The laser threshold dependence on the operating wavelength can be explained as follows. The increase of the “blue” laser wavelength is due to an increase of the In atom concentration in the active layers, which results in a composition inhomogeneity (In-rich clusters, quantum dots and discs) and apparently in increasing nonradiative defect concentration leading to an intensity decrease and broadening of the emission spectra and, thus, to an increase of the laser threshold. From other side, a considerable decrease of In atoms in the active layer promotes the InGaN band gap rise thus diminishing the band offset. It was found that many growth parameters influence the laser wavelength such as In content in the gas phase, the growth temperature, the quantum well thickness, the total flow through the reactor and reactor pressure during the quantum well stack growth as well as the V/III gas ratio during the growth of the barriers in MQW. For example, the higher the V/III gas ratio is the longer the laser wavelength becomes (Fig. 2).

One of the most discussed problems for the GaN-based lasers is the mechanism of the optical gain: localised or delocalised states play a dominant role in the

mechanism. In order to make account in the problem, a series of measurements of the PL, PLE and laser spectra at RT as well as of the temperature dependencies of the laser spectra and thresholds were carried out. Comparison of the laser, PL and PLE spectra for “violet” (430 nm) and “blue” (450–470 nm) lasers at room temperature showed that the laser line positions are near to the mobility edges of the quantum wells, and thus the role of the localised states at high temperatures is insignificant for these MQW heterostructures.

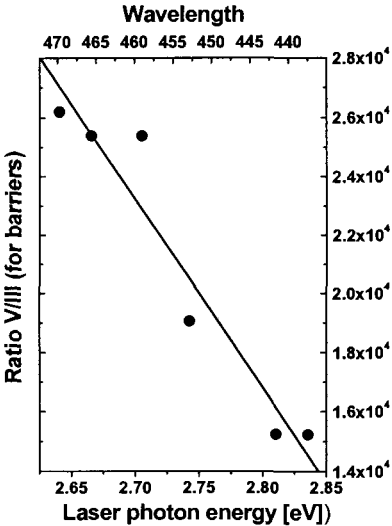


Figure 2. Influence of V/III ratio on wavelength and photon energy of InGaN/GaN MQW lasers.

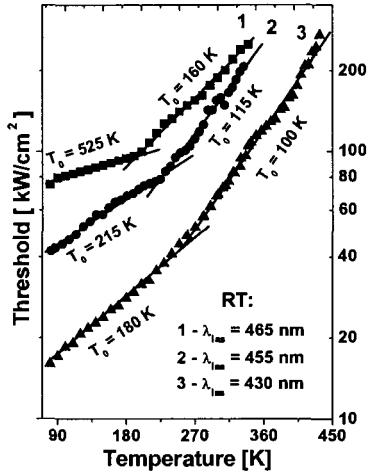


Figure 3. Temperature dependence of laser threshold of three InGaN/GaN MQW lasers.

In order to reveal a possible difference between the laser mechanisms i n the short- and long-wavelength lasers, their laser thresholds were measured as a function of temperature. Fig. 3 presents the temperature-resolved laser thresholds of three InGaN/GaN MQW heterostructures operating at $\lambda_{las} = 430$ nm, 455 nm and 465 nm at $T = 300$ K. The temperature dependence of the laser thresholds for $T = 80 - 450$ K for all MQWs lasers showed two slopes with an inflection point nearby 200 - 250 K. The “violet” and “blue” lasers had characteristic temperatures from $T_0 = 180$ K up to $T_0 = 530$ K for the low temperature range and $T_0 = 100 - 160$ K at high temperatures.

The alteration of the characteristic temperature values may be attributed to a change in the gain mechanism. It can be admitted that in the low temperature interval of 80 - 220 K, the most important account to the gain mechanism is given by the localised states created by In-rich clusters (quantum dots). The characteristic temperature of the “blue” lasers $T_0 = 530$ K is much higher than the maximal value for merely one-dimensional confinement $T_0 = 285$ K [12].

An influence of the excitation intensity on the laser spectrum structure and position, laser power and efficiency as well as on the luminescence characteristics was investigated at room temperature. The laser mode position shifts first to the long wavelength side with an I_{exc} rise, and then it moves to shorter wavelengths (Fig. 4, curves 1,2). The mode behaviour may be explained by a competition and superposition of several effects: an increase of the refractive index due to the active layer heating, a decrease of the refractive index owing to the high concentration of the electron-hole plasma and an alteration of the optical confinement factor.

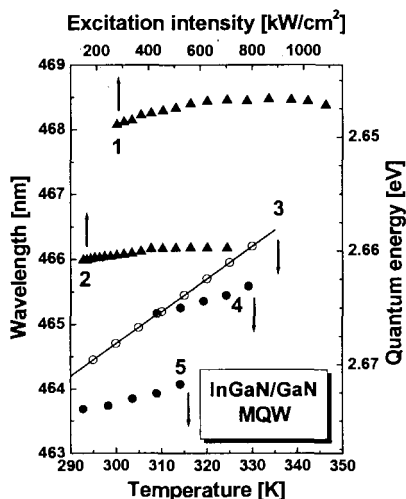


Figure 4. Excitation intensity (1,2) and temperature dependencies of laser modes (4, 5) and total laser spectrum (3) positions.

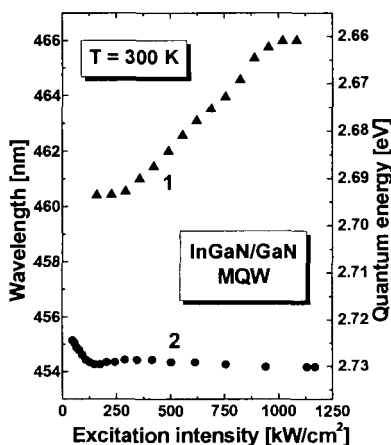


Figure 5. Spectral position of the laser (1) and PL (2) spectra as a function of excitation intensity.

In order to understand the reasons of the laser spectra shift with excitation intensity and in order to reveal influence of the exciting and inherent light on the laser mode structure and position, measurements of the PL and laser spectra at excitation by a narrow stripe and by the focused radiation of the N_2 laser were carried out (Fig. 5) and compared to the temperature dependencies of the laser spectra (Fig. 4, curves 3-5). It was shown that the PL peak position shifts only to the high energy side at the same time when the laser lines move to the low energies. On the base of these results, it was concluded that the large shift of the laser spectrum in the I_{exc} interval of 100 – 1000 kW/cm^2 is due to a considerable thermal overheating of the active region which is in turn exclusively caused by the inherent InGaN/GaN laser radiation. The maximal value of the overheating reaches 40 - 100 K depending on the cavity quality and also the laser light density inside the cavity.

4 InGaN/GaN MQW electroluminescence test heterostructures

Fig. 6 presents the current density dependence of the EL peak position (curves 1-3) of three ELT structures at DC excitation: with SiO₂ mask and without copper plate (1), with SiO₂ mask and with copper plate (2), without SiO₂ mask and with copper plate (3). Curve 4 shows the same dependence for the first device under pulse excitation. Line 5 shows the EL spectra peak position of the first device in temperature interval T=300 - 380 K at J = 100 A/cm².

The EL spectra shift to the high energy side with a current density J rise up to J = 100 A/cm² which is attributed to filling of the localised states. It was shown that the reason for the red shift with the further J increase is heating of the active layer region which is the highest for the first sample with low heat sink. At the same, time the pulse current does not lead to a significant heating of the structure. The temperature coefficient of the EL spectrum shift (curve 5) is of about 0.2 meV/K. It allowed us to estimate the temperature overheat of the ELT active region in comparison to the pulse excitation.

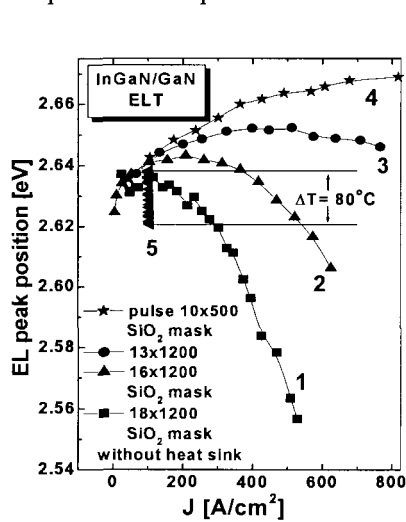


Figure 6. Current density dependence of the EL peak position at CD (1-3) and pulsed current (4) excitation. 5 - temperature shift of the peak position.

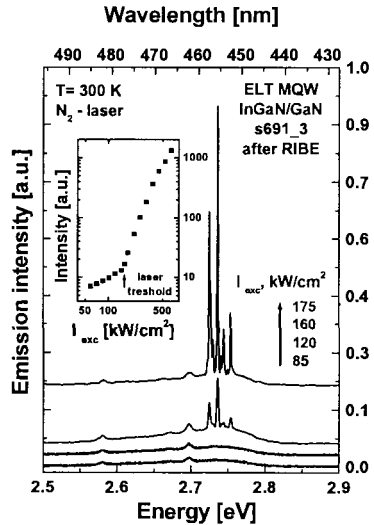


Figure 7. PL and laser spectra from cavity edge at different I_{exc} and input-output characteristic (inset).

Laser action was achieved in this structure under optical excitation. Fig. 7 shows PL and laser spectra of the structure at different excitation intensities. The laser threshold was of about 170 kW/cm² in this case. The laser wavelength was near 455 nm. Such a sufficiently low threshold of the laser operating in the blue region evidences the high quality of the quantum wells.

Acknowledgements

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CARBON NANOTUBES IN MICROELECTRONIC APPLICATIONS

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Carbon nanotubes with their outstanding electrical and mechanical properties are suggested as an interconnect material of the future and as switching devices, which could outperform silicon devices. In this paper we will introduce nanotubes, specify the applications, where nanotubes can contribute to the advancement of Moore's law and show our progress of nanotube process integration in a microelectronic compatible way. The growth of single individual nanotubes at lithographically defined locations on whole wafers as a key requirement for the successful implementation of nanotubes is shown. In terms of nanotube transistors we propose a vertical nanotube transistor concept which outperforms the ITRS requirements for the year 2016. The performance is mainly limited by contact resistances, but by comparison with silicon devices we show that fabricated nanotube transistors already today exceed the values for transconductance, on-resistance and drive current of silicon devices.

1 Introduction

Carbon nanotubes (CNTs) are a 12 years ago discovered form of carbon, which can be thought of as a rolled-up sheet of hexagonal ordered graphite formed to give a seamless cylinder. They can be 0.4 – 100 nm in diameter with lengths up to 1 mm. Several single-walled nanotubes (SWCNTs) can be concentrically nested inside each other, like a Russian doll, forming so-called multi-walled carbon nanotubes (MWCNTs). Due to the variety of extraordinary properties exhibited by carbon nanotubes, a large number of possible applications have been proposed [1]. In particular, the high current carrying capacity and mechanical stability of metallic nanotubes indicate applications in microelectronic interconnects [2] whereas the reasonably large band gap of narrow single-walled nanotubes suggests their use as nanoscale transistor elements [3].

When we think about alternative approaches for the fabrication of microelectronic circuits, a pre-condition for new materials is, that they have to outperform the current technology. In principle this is true for CNTs, but one of the major hurdles to overcome, is the targeted placement of a specific CNT with prescribed character, i.e. MWCNT or SWCNT, diameter and chirality. The latter determines whether a SWCNT is metallic or semiconducting. Therefore, the progress in CNT-science has shifted in recent years from a mere scientific understanding to integration issues [4,5]. Here we describe our approach to grow

nanotubes on a wafer exactly where we want them to be, establishing the most advanced integration scheme for CNTs. We divide the applications in two sections, where one is devoted to the interconnect-topic, i.e. the on-chip wiring of the conventional transistors, and the other is device-related, where SWCNTs are used as switching devices.

2 Nanotubes in interconnect applications

If we look at the cross-section of a typical chip like in Fig. 1(a), we see that nowadays chips have become “all wire”. The transistors at the bottom make up only a fraction of the total chip, and already today, the speed and performance of such chips is mainly limited by the interconnects, i. e. the copper-based wiring of the transistors with different metal layers (wires) and the vertical connections between these layers, which are termed via. These vias are prone to electromigration failures as can be seen in Fig. 1(b). The arrows mark regions, where voids have formed due to the high current densities in these structures. In 2013 the ITRS [6] predicts a current density of $3.3 \cdot 10^6$ A/cm² in a via, a value which, to date, can only be supported by CNTs, where current densities exceeding 10^9 A/cm² have been reported in nanotubes without heat sinks. At this ITRS technology node a MPU/ASIC half-pitch of 32 nm is predicted. On this scale, traditional interconnect schemes become problematic due to the increased wire resistances resulting from grain and surface scattering effects and the higher current densities which must be carried [7]. Sufficient heat removal from the chip is already a problem in present day computers. Due to their superb thermal conductivity, which exceeds that of

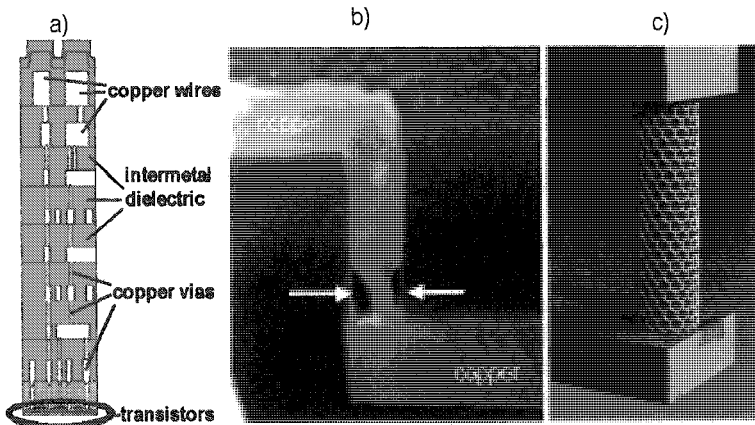


Figure 1. a) Cross-section through a typical chip, which consists mainly of copper-wires and -vias. b) Copper-via connecting two different metallisation levels in chip. The arrows indicate electromigration induced failures. c) Proposed CNT-via, which should withstand a 1000 times higher current density.

diamond by a factor of two, nanotubes may also help to remove the heat more efficiently from the chip. Therefore we propose CNTs, as shown in Fig. 1(c), to realize such critical vias and contact holes.

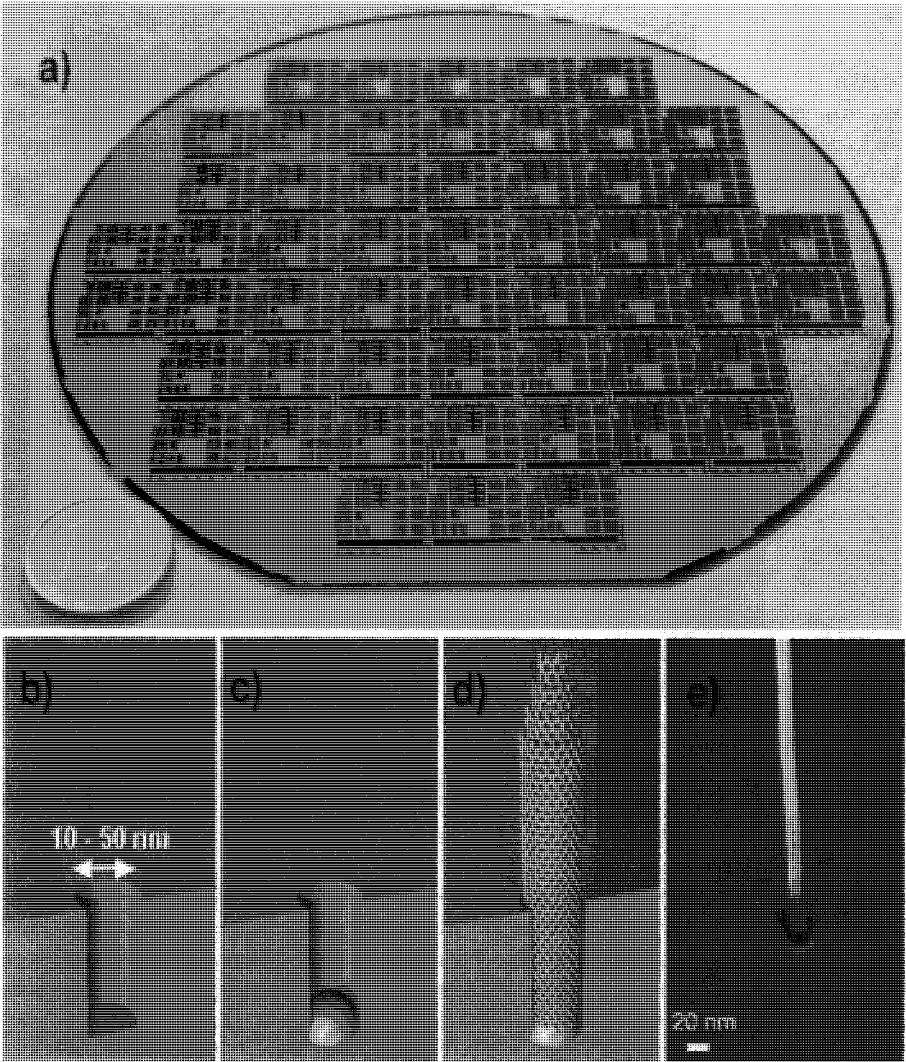


Figure 2. a) A 6-inch wafer with CVD-grown CNTs at lithographically defined locations. b)- c) In a 10-50 nm wide nano-hole a catalyst is deposited and MWCNTs are grown. e) A single MWCNT of 20 nm diameter protruding from a nano-via.

We have already indicated in [2], that such interconnects outclass conventional copper metallization at this reduced dimension with respect to electrical resistance and current carrying capacity.

Substantial progress has been made in the recent year by demonstrating the lithographically defined growth of CNTs on wafer-scale and the growth of individual MWCNTs in nano-vias, which have been created by conventional lithography and dry-etching methods. In Fig. 2(a) the black structures on the 6-inch wafer consists of MWCNTs, which are grown in situ using an iron-based catalyst and hydrogen-acetylene mixture as a carbon source. In Fig. 2(b)-(d), the process flow to fabricate individual CNTs at lithographically defined locations is sketched. Conventional i-line lithography in combination with a spacer-technique is used to create nano-vias with 10-60 nm diameter [8]. After the deposition of an iron-based catalyst at the bottom of the via, a single MWCNT can be grown out of the via. This can be seen in Fig. 2(e), where a 20 nm diameter MWCNT protrudes out of the nano-via. It has been observed that the diameter of the tube adjusts automatically to the diameter of the hole [8], which results in a filling factor of the via of 100%.

Challenges within this approach lie in the deposition and material of the catalyst, limited temperature budget in combination with high quality requirements for the CNTs, which normally need temperatures above 600°C to get structurally and electrically adequate results.

3 Carbon nanotubes in transistor applications

If a semiconducting SWCNT of about 1 nm diameter is attached to two separated (metallic) contacts (source and drain), a near by third gate-electrode can modulate the conductivity of the tube by about 6 orders of magnitude at room temperature. This effect has been observed already in 1998 and has led to a kind of race in the scientific community to achieve the best performing CNT-device [3,4,5]. Although it is not yet clear, how the device actually works, the most recent work [5] can be fairly explained by the assumption of simple 1-dimensional electrostatics [9], which relates the charge in the tube by the capacitance of the tube- and gate structure and the applied gate-voltage. Based on this theory a best performance projection for CNT-transistors can be made and compared to the ITRS requirements of the year 2016. We propose a vertical, coaxially gated nanotube transistor [10], as shown in Fig. 3(a), with a 1 nm diameter tube, 10 nm gate-length and a 1 nm thick silicon dioxide as the effective gate-oxide. In order to compare with ordinary silicon devices, which are always scaled to device width, we make a parallel array of this device comprising 250 CNTs per micron, as shown in Fig. 3(b). With the theory of Guo et al. [9] we can estimate the performance of the CNT-transistor and the results are listed and compared with the ITRS in Table 1.

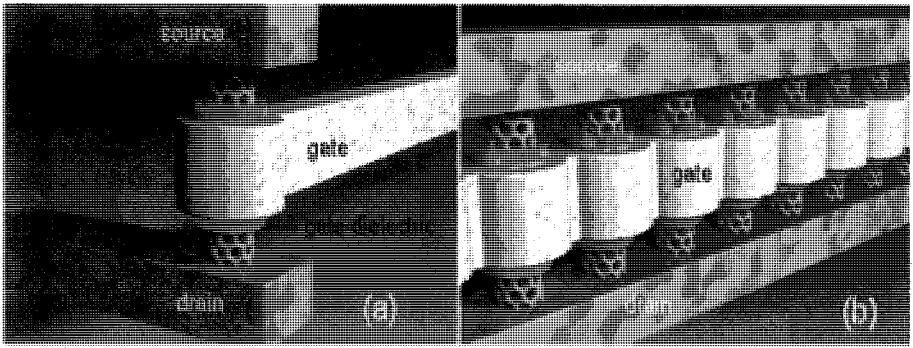


Figure 3. Proposed vertical coaxially gated CNT-transistor in a single (a) or parallel array (b) CNT-transistor.

It clearly can be seen that the CNT-transistor fulfills all the requirements by far. The drive current at the supply voltage of $V_{dd}=0.4\text{ V}$ is almost twice as high, the transconductance g_m is almost 15 times higher, while the gate-delay t is almost half of the allowed value. The subthreshold swing S is close to the theoretical limit, the leakage current is $\frac{1}{4}$ of the allowed value and can be adjusted by the gate-material. The allowed effective equivalent gate-oxide thickness of 1 nm is well in the range of low gate leakage and manufacturability.

These promising values leave room for performance loss due to deviation from the ideal behavior. The main contribution in the performance loss comes from neglecting the contact resistance, which arises between the metallic contacts and the carbon nanotube and is caused by k-vector mismatch and/or Schottky-barriers. In the following we model this resistance as linear, i.e. ohmic resistance and calculate the performance dependence on the contact resistance. The extrinsic transconductance g_m can be calculated from the intrinsic transconductance g'_m and the extrinsic output conductance g_{ds} and is given by:

$$g_m = \frac{g'_m (1 - g_{ds}(R_s + R_d))}{(1 + g'_m R_s)}$$

Tabel 1. Comparison of the year 2016 ITRS requirements with the properties of the proposed vertical CNT-transistor array.

	Vdd Volt	drive current $\mu\text{A}/\mu\text{m}$	trans- conductance $\mu\text{S}/\mu\text{m}$	$t (C_{\text{gate}} \cdot V_{\text{dd}}/I_{\text{dd}})$ (ps)	S mV/dec	leakage $\mu\text{A}/\mu\text{m}$	effective tox (nm)
ITRS Year 2016	0.4	1500	1000	0.15	70	10	0.4- 0.5
CNT-FET	0.4	2500	15000	0.08	65	2.5	1

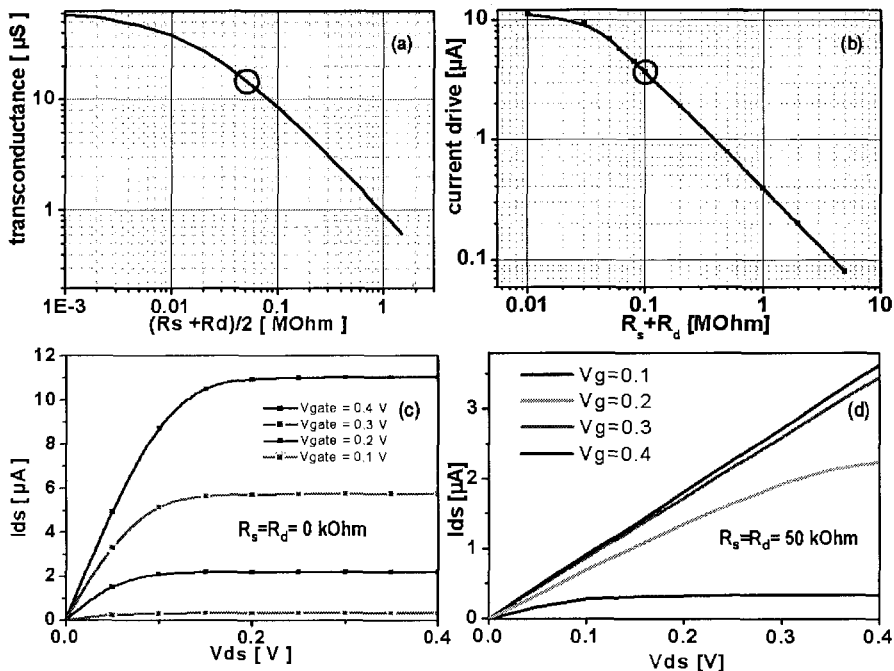


Figure 4. (a) The extrinsic transconductance g_m as a function of symmetrical contact resistances. (b) The decrease of drive current versus contact resistance. (c) The ideal transistor characteristic compared to (d), where a contact resistance of 50 kOhm is assumed. The circles in (a) and (b) denote the respective values for the case of $R_s = R_D = 50$ kOhm.

The situation is summarized in Fig. 4, where the dependence on drain- and source-contact resistances, denoted by R_D and R_S , for the extrinsic transconductance and the current drive is shown. Experimental values for the individual contact resistances range between 30 kOhm and 2 MOhm. For an assumed resistance of 50 kOhm, the change of the ideal characteristic to that of the non-ideal, is depicted in Fig. 4(c) and (d) and the influence on the transconductance and drive current is indicated by circles in Fig. 4(a) and (b).

The proposed CNT-transistor can fulfill the ITRS requirements even with these reduced performance values. If we take into account, to scale the transistor not only by width, but by the used area, as shown in Fig. 5, we can imagine a 2-dimensional vertical array of individual nanotubes, creating a very promising device. If we compare this CNT-device with the silicon world, we have to keep in mind that the silicon device needs area for source and drain contacts and is not stackable. Whereas our proposed CNT-transistor incorporates already source and drain contacts and is stackable. So, with this concept, we can create real 3-dimensional electronics.

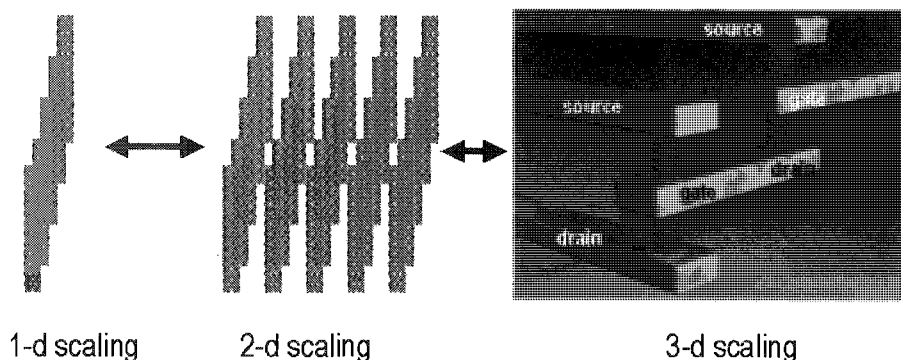


Figure 5. Different scaling scenarios for comparing nanotube transistors with the silicon world. The comparison should include the scaling to the used area, which favors 2-d scaling, and the option to make real 3-d electronics.

To top off the discussion, we compare the current status of real fabricated nanotube transistors with the best performing silicon transistors in Table 2. After the forgoing discussion, we think that it is justified to scale the transistor properties by the device width. The CNT-FET of [11] uses electrolyte gating and can be seen as a limiting case for CNTs regarding the use of high-k dielectrics. It should be noted that we have listed only properties responsible for the static performance of the devices, as the gate-scaling is not yet as advanced as in the silicon world.

The next question to be answered for these superior CNT-transistors is what will happen with these outstanding performance values at a gate-length of 10 nm?

Table 2. Comparison between fabricated nanotube and silicon transistors.

	p-CNT FET [11] 1.4 μm (1 V) Rosenblatt (2002)	p-CNT FET [5] 3 μm (1.2 V) Javey (2002)	MOSFET[12] 0.1 μm (1.5V) Ghani (1999)	FinFET [13] 10 nm (1.2V) Yu (2002)	MOSFET[14] 14 nm (0.9V) Doris (2002)
drive current I_{ds} (mA/ μm)	2.99	3.5	1.04 nFET 0.46 pFET	0.450 nFET 0.360 pFET	0.215 pFET
transconductance $\mu\text{S}/\mu\text{m}$	6666	6000	1000 nFET 460 pFET	500 nFET 450 pFET	360 pFET
S mV/dec	80	70	90	125 101	71
on-resistance Ohm/ μm	360	342	1442 nFET 3260 pFET	2653 nFET 3333 pFET	4186 pFET
gate- length nm	1400	2000	130	10	14
normalized gate- oxide 1/nm	80/1 = 80	25/8 = 3.12	4/2 = 2	4/1.7 = 2.35	4/1.2 = 3.33
mobility $\text{cm}^2/(\text{Vs})$	1500	3000	--	--	--
I_{off} (nA/ μm)	---	1	3	10	100

Acknowledgements

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QUANTUM-CONFINED IMPURITIES AS SINGLE-ATOM QUANTUM DOTS: APPLICATION TO TERAHERTZ EMITTERS

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This work will argue that impurities within semiconductor crystals can be thought of as the ultimate in quantum dots, with the three-dimensional confining potential being provided by a single atom and localizing single electrons or holes. Rather than being limited to the impurity species and the energy levels provided by nature, a heterostructure confining potential provides a means to tune the energy levels of the impurities. More importantly, unlike self-assembled quantum dots, which suffer from significant inhomogeneous broadening due to the variation in dot size, quantum well systems with these embedded quantum dots can be fabricated to very high qualities with contemporary molecular beam epitaxy growth techniques. In this work the first steps to utilizing internal transitions of these single atom quantum dots to develop Terahertz lasers are reported. These include time resolved measurements of the excited impurity state lifetimes performed at the Dutch free-electron laser.

1 Introduction

There is a concerted effort amongst the scientific community to develop compact, low input power sources of far-infrared (30-300 μm) or Terahertz radiation (1-10 THz), for a summary of recent work see for example [1-3]. One particular thrust centers around extending the wavelength of the highly successful mid-infrared quantum cascade lasers, again see the literature [4-7] for background. The latter has been successful in pushing the emission wavelengths towards 20 μm [8]

and beyond [9], and following weak electroluminescence at 88 μm [10] and 40 μm [11], a laser was reported at the beginning of 2002 [12].

Theoretical papers, see for example [6], suggest that sustaining a population inversion at very long wavelengths (low intersubband energy separations) may be difficult. This is because although the intersubband electron–longitudinal optic (LO) phonon scattering, in III-V materials, is reduced when the subband separation is less than the LO phonon energy (36 meV in GaAs which implies emission wavelengths greater than 35 μm), intersubband electron–electron scattering increases and becomes the main non-radiative loss channel. In addition, as the temperature increases thermally activated LO phonon emission also continues to increase which eventually destroys the population inversion [13].

The purpose of this work is to propose an alternative route to intersubband transitions as a means of generating Terahertz photons – a route which could circumvent the detrimental non-radiative scattering processes outlined above.

2 Intersublevel versus intersubband transitions

The one-dimensional confining potential characteristic of semiconductor heterostructures (quantum wells) leaves two degrees of freedom in the bound state of the motion of electrons (or holes). This movement in the plane of the quantum wells gives rise to ‘subbands’ in the energy-momentum curves, see left hand diagram of Fig. 1.

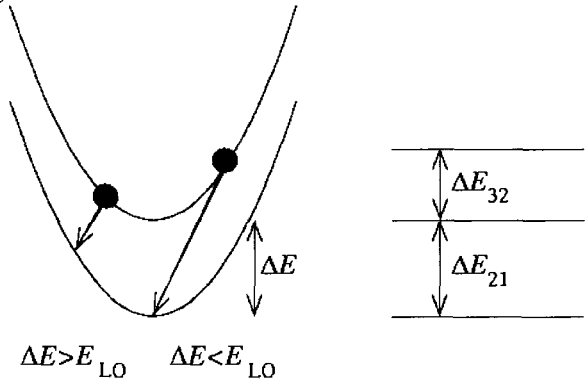


Figure 1. Comparison of intersubband transitions (left) as found with one-dimensional confining potentials as in quantum wells, with intersublevel transitions akin to three-dimensional confining potentials as found in quantum dots.

The Fermi-Dirac distributions of carriers within the subbands means that even when the subband separation is less than the energy of an LO phonon, an electron (or hole) with sufficient in-plane kinetic energy in the upper subband can still emit an LO phonon. Although this effect decreases with temperature and subband separation, it is nonetheless present and competing with radiative transitions and as

it increases with temperature it could be the limiting mechanism for high temperature performance of cascade lasers [13]. In addition, any population inversion is also fighting against the losses through electron–electron (or hole–hole) scattering, which increase as the subband separation decreases [14]. Both these points serve to illustrate that sustaining a population inversion between two quantum well subbands separated by a Terahertz frequency energy gap will be difficult.

The idea therefore is to use transitions between the discrete dispersionless sublevels obtained with three-dimensional (quantum dot) confining potentials, as illustrated in the right hand diagram of Fig. 1. Now if the energy separations are designed not to be equal to the LO phonon energy of 36 meV (in GaAs), then intersublevel scattering due to single LO phonon emission is completely suppressed, rather than just reduced as in the case of quantum well intersubband transitions. In addition, if the density of carriers within a single dot is kept low, then carrier–carrier scattering will also be reduced. In fact, the main non-radiative loss mechanism is likely to be much weaker (and slower) multiple-acoustic phonon scattering. Thus, it might be expected that the lifetime of a carrier in an excited state of a quantum dot is much longer than in a quantum well, which suggests it will be easier to maintain a population inversion in the former.

3 Realising three-dimensional confining potentials

The obvious material system that springs to mind when a desire for three-dimensional confining potentials arises, is that of InAs/GaAs self-assembled quantum dots. Although progress in realizing devices in these materials has been great, they are still a subject to large distributions in sizes and hence significant inhomogeneous line broadening [15]. As a fraction of the emission energy, this line broadening is very severe when far-infrared emitters are considered.

Impurity atoms in semiconductors have many similarities to self-assembled quantum dots, for example, the charge carriers are still localized in all three-dimensions, there are discrete (dispersionless) energy levels and through the use of an additional heterostructure potential (embedding the impurities in a quantum well) they are structurally tunable. In addition to this the Bohr radius of a typical impurity can be as low as 2 nm and they naturally store just one electron or hole (so doping is not a problem). Furthermore, given that they are merely δ -doped quantum wells, their growth is highly reproducible and of high quality – they are not plagued by large linewidths. Perhaps most importantly for the applications of interest here, the sublevel separations are in the far-infrared or Terahertz region of the spectrum.

4 Picosecond spectroscopy of Be acceptors in GaAs

Given the interest in providing an alternative technology to intersubband transitions in quantum wells for the generation of far-infrared and Terahertz radiation, the impurity of Be in GaAs/AlGaAs heterostructures was employed. The reasons being that heterostructures in this material system are easily obtained to very high quality and the binding energy of the Be acceptor in bulk material is 28 meV, which is deep in the Terahertz energy band (1–10 THz is equivalent to 300–30 mm, which has photons of energy 4–41 meV). Workers in Russia have similar aims however they have focused on group IV materials and are using strain rather than a heterostructure potential to tune the energy levels, see for example [16,17].

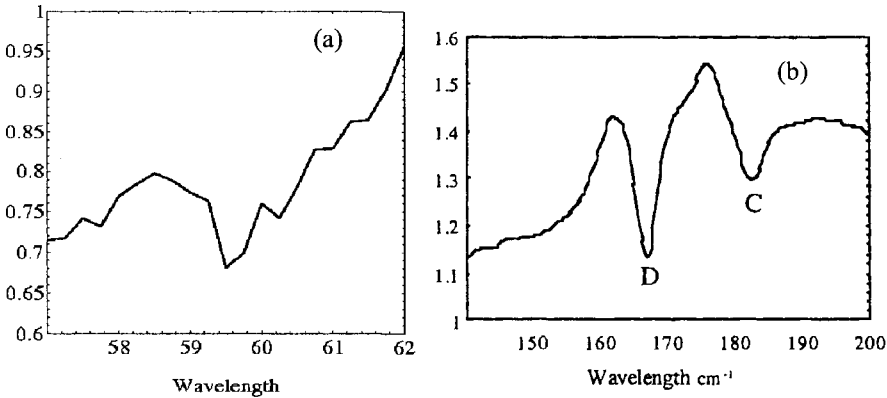


Figure 2. Low temperature (a) linear (wavelength in mm) and (b) FTIR absorption spectra of Be-doped GaAs.

Fig. 2(b) shows the results of fourier transform infrared (FTIR) absorption measurements on Be-doped bulk GaAs. This spectra was taken in normal incidence thus illustrating the three-dimensional nature of the confinement and shows two features corresponding to the C and D components of the 1s–2p transition at 184 and 167 wavenumbers respectively (corresponding to 54 and 59 mm, note the 2p–1s energy separation is 3/4 of the 28 meV binding energy for Be in bulk).

In order to measure the lifetime of the 2p state the samples were studied using the Dutch free electron laser FELIX, for experimental details of these measurements see [18]. Both lines exhibited some saturation under excitation by the free electron laser and the recovery of the absorption was measured using the balanced pump-probe technique [19]. This technique uses two probe pulses, one preceding and one following the pump pulse; the resulting balance between the two pulses is taken as the pump-probe signal. The high sensitivity of this technique allows absorption changes of 0.5% or even less to be detected and is essential for the measurements described here.

Simple three level fits to the observed pump-probe signal for the two absorption lines in Fig. 2(b) (at a sample temperature of 4.2 K) indicated decay lifetimes of 350 and 360 ps for the C and D lines respectively. These figures are two orders of magnitude longer than the equivalent intersubband lifetime in quantum well systems. Furthermore, measurements up to 60 K showed that this lifetime was quite insensitive to temperature [20]. Both qualities offer great potential for a population inversion of the 2p level over the 1s level and hence show the promise of a solid-state source of Terahertz radiation.

Goswami [21] (p. 476) gives the 2p–1s radiative decay rate for a hydrogen atom, which is proportional to the square of the effective mass and inversely proportional to the permittivity of the material and the cube of the transition energy. Thus, it may be expected that the radiative lifetime of impurities emitting in the far-infrared (low energy) region of the spectrum will be much longer than atomic systems emitting in the visible and ultraviolet. Indeed this is the case and taking the low frequency relative permittivity of GaAs as 13.18, the heavy-hole effective mass as 0.62 and the wavevectors 183 and 167 inverse cm of the Be C and D lines respectively, gives the lifetimes for spontaneous radiative emission as 87 and 117 ms. These values are clearly much longer than the lifetimes measured and hence the experimentally observed lifetimes are due to some non-radiative processes. The 2p–1s energy separations measured in Fig. 2 are 167 and 184 wavenumbers which are equivalent to around 21 and 23 meV respectively. These values are much less than the LO phonon energy of 36 meV in GaAs, thus holes in the 2p impurity state cannot emit LO phonons and collapse to the 1s ground state. The times themselves are also somewhat longer than typical intersubband acoustic phonon scattering events, and when coupled with the relatively large transition energies (compared to typical acoustic phonon energies) suggest the measured lifetimes are limited by multiple acoustic phonon scattering processes.

5 Picosecond spectroscopy of Be acceptors in GaAs/AlAs multiple-QWs

Recent measurements [18] have extended this work to consider the manipulation of the impurity levels with a quantum well potential. GaAs/AlAs multiple quantum wells doped with Be were grown and the structural tunability of the impurity levels was demonstrated by an increase in the 1s–2p absorption energy.

Similar pump-probe measurements as above were performed for a range of temperatures as illustrated for one particular sample in Fig. 3(a). Curve fitting implies that the 2p excited state lifetime is around 80 ps. This is a factor of 4 less than that measured for bulk and cannot be explained by the very small change in the radiative lifetime. The only explanation for this dramatic reduction in the lifetime is the zone-folding effect of the multiple quantum well potential on the acoustic phonon modes. Rather than relying on multiple phonon events or phonons of very large momentum, the zone-folded phonon spectrum could provide relatively low momentum phonon modes with energies larger than that in the bulk. These modes

which are particular to the multiple quantum well symmetry lead to enhanced non-radiative scattering and hence a reduced excited state lifetime. The temperature dependence of the excited state lifetime is also very important. It does not change up to 60 K and offers hope that emission from these states could exist up to liquid nitrogen temperatures at the very least.

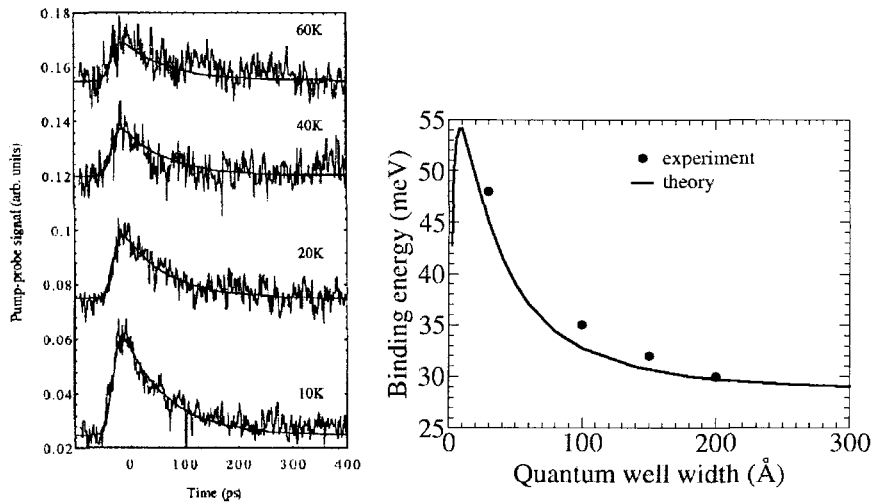


Figure 3. (a) Temperature dependence of pump-probe signal from the Be D-line transition in a multiple quantum well sample, the fitted curves all correspond to a decay of 80 ps (b) Be acceptor binding energy as a function of the quantum well width.

Fig. 3(b) shows the measured binding energy of the Be acceptors as a function of the quantum well width for a series of samples [22]. The data are in very good agreement with theoretical calculations [14] and show that the 1s–2p energy separation (which is around 3/4 of the binding energy) can be tuned from 21 meV for bulk to a maximum of around 42 meV at narrow well widths.

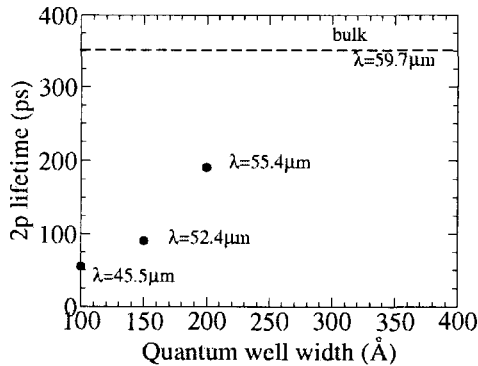


Figure 4. The dependence of the lifetime of the Be 2p state on the quantum well width.

Fig. 4 shows that the lifetime of the 2p impurity level decreases monotonically with the quantum well width. This is likely to be due to the increasing overlap between the impurity state and the confined acoustic phonon modes.

6 Summary

It has been shown that the binding energy of a Be acceptor can be varied from its bulk value of 28 meV to a maximum of around 55 meV in a narrow GaAs/AlAs quantum well. The corresponding separation of the impurities' internal 1s and 2p levels is around 21 to 42 meV, which is equivalent to a wavelength of between 60 and 30 nm. Pump probe spectroscopy of the same samples has shown that the lifetime of the upper (2p) level varies from around 350 ps in bulk material to 80 ps in the narrowest quantum well. This variation in lifetime is thought to be due to non-radiative scattering due to zone-folded acoustic phonon modes, which arise from the symmetry of the multiple quantum well potentials.

These lifetimes are, however, considerably longer than the sub-picosecond lifetimes typical of quantum well intersubband transitions of similar energy separation. This will aid the build up of a population inversion on the excited impurity states. In addition, the temperature stability of the intra-impurity lifetime (as measured up to 60 K), suggests that the use of the quantum dot properties of semiconductor impurities might provide a route to obtaining temperature stable far-infrared lasers.

Acknowledgements

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InGaN/GaN QUANTUM WELL HETEROSTRUCTURES GROWN ON SILICON FOR UV-BLUE LASERS AND LIGHT EMITTING DIODES

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Research results on optical, laser, electroluminescent and structural properties of InGaN/GaN MQW heterostructures grown on silicon substrates are presented. Concentration of In in QWs and the thickness of the layers were estimated from X-ray diffraction measurements. For the first time, laser action under optical excitation was obtained for $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}/\text{Si}$ MQW heterostructures ($x = 0.151$, $J_{\text{thr}} = 40\text{--}80 \text{ kW/cm}^2$ at room temperature, $T_{\text{max}} = 630 \text{ K}$, $P = 10 \text{ W}$, $E = 80 \text{ nJ}$).

1 Introduction

GaN-based compounds are very promising for light emitting diodes (LED) and laser diodes (LD) operating in the ultraviolet-orange spectral region [1]. The GaN-based LEDs grown on sapphire substrates become as bright and efficient as incandescent bulbs. However, especially for applications in high-volume low-cost market segments, the choice of substrate is an important question. Sapphire suffers from a low thermal conductivity. Silicon is a promising alternative substrate for GaN growth because of its low cost, excellent quality, large-area availability and the possibility to integrate GaN-based light emitting devices and high-power electronics with Si-based photodetectors and logical circuits. The growth of high-quality crack-free GaN on silicon, owing to the high mismatch in lattice constants and in thermal expansion coefficients of GaN and Si, requires a sophisticated growth procedure

employing a combination of high and low temperature AlGaIn layers and more than one nucleation step [2]. A comprehensive investigation of structural, optical and electrical properties of the heterostructures grown on Si, which the work is devoted to, can lead to better understanding of physical reasons of the existing problems, to establish a feedback with technology and to create the UV-visible LEDs and LDs with characteristics comparable to that for structures grown on sapphire [1,3].

2 Experimental

InGaIn/GaN multiple quantum well (MQW) heterostructures were grown in AIXTRON MOVPE reactors on (111)-oriented n-type Si substrates at low pressures (200 mbar or 50 mbar). Trimethylgallium (TMGa), trimethylaluminum (TMAI), trimethylindium (TMIn), ammonia (NH_3) and silane (SiH_4) were used as precursors. The structures were free of cracks. The layer design was the following: GaN /3×(InGaIn/GaN/GaN:Si(600 nm)/(strain reducing layer stack)/Si. The electroluminescence test heterostructures (ELT) had thick doped GaN:Mg and GaN:Si cladding layers and an electron blocking AlGaIn:Mg (10 nm) layer.

Electroluminescence was excited by voltage imposed to the ELT samples by stripe contacts. Photoluminescence (PL) and lasing were excited at $T=18\text{--}500\text{ K}$ by the radiation of a N_2 laser ($h\nu=3.68\text{ eV}$, $f=1\text{ kHz}$, $\tau_p=8\text{ ns}$) and a CW HeCd laser ($h\nu=3.81\text{ eV}$). The X-ray diffraction was measured with a Philips X'Pert Materials Research Diffractometer. The system uses CuK_α radiation and a four-crystal Ge monochromator in the (220) setting. It is also equipped with an X-ray mirror in order to increase the intensity of the primary beam. The beam size was limited to $1.4\times3\text{ mm}^2$, $\omega - 2\theta$ scans were performed using a triple bounce Ge (220) analyser.

3 Results and discussion

The first stage of the investigation consisted of developing high-quality GaN layers grown on silicon. As a result of a thorough study on the effects of the growth conditions and the strain-reducing layer design on the optical properties and surface morphology of the GaN epitaxial layers, GaN layers of good quality were grown. Laser action ($\lambda_{\text{las}}=377\text{ nm}$, $I_{\text{thr}}=700\text{ kW/cm}^2$) under optical excitation in those epitaxial layers was obtained for the first time for GaN/Si [4]. After that the InGaIn/GaN MQW layer stack was grown. For the first time, laser action under optical excitation was obtained for such a type of heterostructure. The laser threshold value was $I_{\text{thr}}=40\text{--}80\text{ kW/cm}^2$, the pulse power was about 10 W. PL spectra at different excitation levels from the surface of a sample and a laser spectrum from the sample edge are depicted in Fig. 1. Carrier recombination and gain mechanisms have been studied on the basis of the investigation of the PL and laser properties in the temperature interval from 18 K to 630 K.

Additionally, ELT MQW heterostructures were grown and studied. Fig. 2, curve 1 shows an EL spectrum under forward bias. The low-energy shift of the EL spectrum comparing to the PL spectra (curves 2-5) evidences a lower carrier concentration at electrical excitation and recombination via localised states in the quantum wells (In rich clusters or quantum dots). At high optical excitation, the delocalised states (electron-hole plasma) play the most important role in the QW emission.

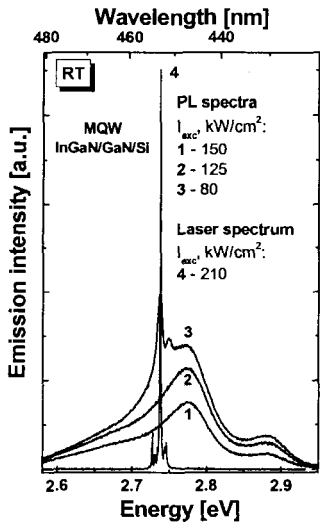


Figure 1. PL (1-3) and laser (4) spectra of InGaN/GaN/Si MQW heterostructure.

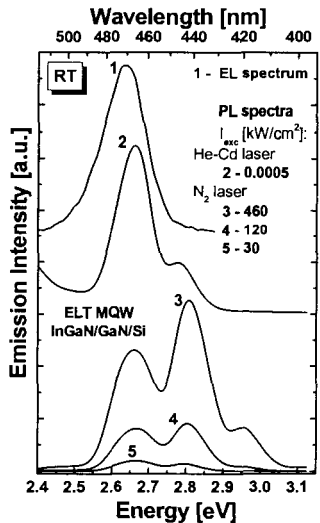


Figure 2. EL (1) and PL (2-5) spectra of InGaN/GaN/Si ELT MQW heterostructure.

InGaN/GaN MQW structures grown on silicon were also studied by structural measurements. The X-ray diffraction pattern taken around GaN (0002) of the sample depicted in Fig. 3 is an evidence of its good quality. The simulation based on the dynamical theory of X-ray scattering shows a reasonable match to the experimental data. This simulation yielded the thickness and compositions of the MQW (3.4 nm In_{0.151}Ga_{0.849}N + 3.9 nm GaN). For the parameter refinement, the relaxation status of the buffer layers was taken into account.

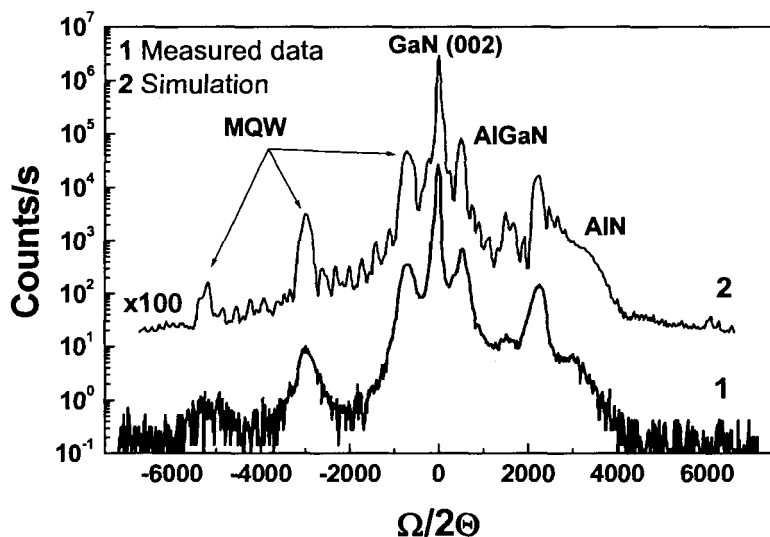


Figure 3. X-ray diffraction pattern of InGaN/GaN/Si MQW heterostructure.

Acknowledgements

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ELECTRICAL PROPERTIES OF *DNA*-BASED SWITCHING DIODE

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Simple model of carrier transport in an active molecular part of *DNA*-based junction, which account for intrinsic and boundary molecular properties has been developed. Exponential dependence of the tunneling transport on the nucleobase number of the *DNA* molecule has been established. The optimal molecular configuration to provide high-speed switching and the temperature regime of molecule junction has been chosen. Junction switching time has been estimated to be characterized by the superexchange carrier transfer time of 10^{-13} s in a wide temperature range.

1 Introduction

Molecular-based electronic devices used as active components in nanoelectronics were recently proposed [1]. The basic function of such devices is a two-terminal molecular junction that can be electrically switched between high- and low-conductance states. Rational design of the switching molecule can be employed to optimize the switching characteristics because they are mainly dependent on the properties of the molecule.

Last experimental and theoretical studies of long-range charge carrier transport in *DNA* molecules showed semiconductor or insulator behavior. The control of high- and low-conductance states can provide an opportunity to develop the switching molecule junction. Charge carrier transport features in *DNA* are mainly defined by the ionization potential of nucleobases and by the energy location of donor and acceptor levels at the molecule termination region [2]. However, the appropriate theoretical approaches as well as the simulation of carrier transport in *DNA* molecules from the point of view of their possible device application were not attended yet. The aim of the paper is to show a simple physical approach for the electrical property simulation of nanoscale *DNA*-based systems.

2 Model

The rising interest in nanoelectronics to *DNA* molecules relates to interchange potential profile of nucleobases with thin barriers corresponding to the distance between neighboring nucleobases $c=0.34$ nm [2]. The potential barrier height in the molecule is defined by the nucleobase sequence and was estimated for the components entering the system by the *ab initio* HF/6-31G method. The

experimental values of ionization potential (IP) [3] and the calculated values of HOMO, LUMO are presented in Table 1.

Table 1. IP, HOMO and LUMO of monomer nucleobases (eV).

	Guanine (G)	Adenine (A)	Cytosine (C)	Thymine (T)
IP exp.	-8.24	-8.44	-8.94	-9.14
HOMO	-8.01	-8.53	-8.96	-9.4
LUMO	4.22	3.63	3.36	3.1

The significant gap values mean an insulator behavior of the *DNA* molecule and detain the charge carrier injection from external contacts. Thus, one has to consider the bound conditions at donor (*d*) and acceptor (*a*) sides of the molecular nucleobase sequence. A molecule configuration which can be interesting is the one where the energy gap between the donor and the molecular bridge approaches to zero at the boundary energy confinement $E_d \geq E_a$. The most experimentally studied molecule configuration is the 5'-*G*-(*A*)_{*n*}-*GGG*-3' nucleobase sequence where excited *G* injects holes toward triplet *GGG* due to the decrease of HOMO at the combination of several identical pairs [4]. The charge carriers injected into the molecular bridge will hopping or tunneling via low potential barriers, which are formed for holes by *A-T* pairs and vice versa for electrons. The charge transport to the acceptor can occur also through a "π-way" of well stacked *DNA*-bases where the energy gap between donor E_d and acceptor E_a is absent, *i.e.* $E_d > E_a$ [2]. The mechanism of such long-distance charge transport is based on the electron transfer theory of superexchange.

Accounting for the potential profile of the nucleobase sequences, a *DNA* molecule can be treated as a periodic system with some potential barriers and wells, which are empty at a non-excited state. The carrier transport in an *N*-period structure can be described by kinetic equations accounting for the carrier concentration in the *i*-th quantum well [5].

The charge carrier hopping term via the *i*-th potential barrier of height ΔE is defined by the concentration of carriers with the significant potential energy that corresponds to $\Delta E \sim k_B T$ and can be written as:

$$g_{a(i)} = \frac{4\pi q m^* k_B T^2 c n (1 - \exp(q V_{bias}) / N k_B T) / h^3}{\int_0^{cn} \exp((\Delta E - \sqrt{q^3 V_{bias} / 8 N \pi \epsilon x}) / k_B T) dx} \tag{1}$$

Here k_B is the Boltzmann constant, *T* is the temperature, *h* is the Planck constant, m^* is the effective electron mass, *c* is the distance between neighboring nucleobases, *n* is the number of nucleobases building the potential barrier and ϵ is the barrier permittivity.

Additionally to the thermally induced hopping the charge carries tunnel through the potential barrier. It can be determined within the Wentzel-Kramer-Brillouin approximation for one dimension as:

$$g_{tun(i)} = \frac{4\pi m^*}{h^3 d} \int_0^E [F(E) - F(E + qV_{bias}/n) D_{WKB}(E)] dE. \quad (2)$$

Here d is the molecule length, $F(E)$ is the Fermi-Dirac distribution function, and $D_{WKB}(E)$ is the tunneling probability, which is described elsewhere [5].

The boundary conditions at the d -DNA bridge and a -DNA bridge correspond to $i=0$ and $i=N$. The number of potential wells and barriers in the structure, their thickness and height are completely defined by the nucleobase sequence.

3 Result and discussion

The kinetic equation system was solved for stationary and time-depend conditions. To simulate the charge carrier transport in the DNA molecule of 5'-G-(A) $_n$ -GGG-3' nucleobase sequence the potential profile between different nucleobases on the basis of the data from Table 1 was accounted.

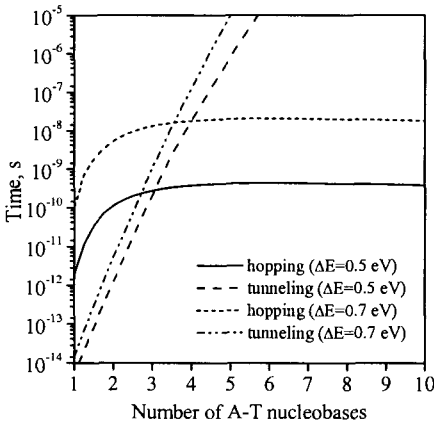


Figure 1. Influence of the nucleobasis number on transfer time.

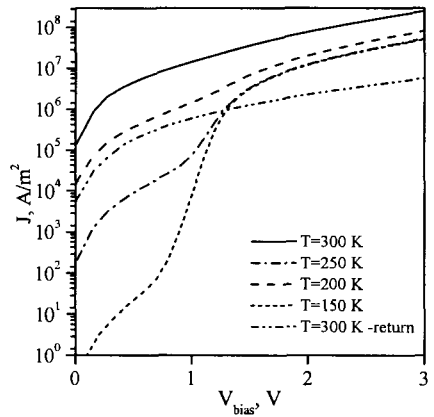


Figure 2. Current-voltage characteristic of 5'-G-(A) $_3$ -GGG-3' DNA molecule.

An important parameter of carrier transport is the transfer time. It was estimated for two different sequences, *i.e.* 5'-G-(A) $_n$ -GGG-3' and 5'-GG-(A) $_n$ -GGG-3' depending on the number of stacked A pairs. The results are presented in Fig. 1. The dominating carrier tunneling up to $n = 4-5$ corresponds to the fast transfer time exponentially slowing down while n increases. The growth of the A sequence number leads to the saturation of the thermally induced hopping time, which is faster for these conditions.

Another interesting feature is that the temperature strongly defines the dominating mechanism of the carrier transport (tunneling or hopping). The behavior of the carrier in a *poly G-poly C* DNA molecule was changed and was almost

linearly dependent on the sequence number due to additional hole hopping from one *G*-nucleotide to another.

The molecular junction behavior at the confinement of bound conditions ($E_d \geq E_a$) can be determined as a regime corresponding to direct propagation of an external signal. Otherwise, the energy gap between donor and acceptor ($E_d \leq E_a$) confines the electron appearance at the acceptor side until equalization of the external bias to the gap. In the standard approach of a diode-transistor logic the combination of molecular junctions in an opposite and non-opposite way provides logic summation and multiplication. The nucleobase sequence can be chosen to have temperature-dependent and temperature-independent regimes. The switching time of a short molecular junction has been estimated to be 10^{-14} - 10^{-13} s that is shorter than that for semiconductor junctions.

4 Conclusion

The model of one-dimensional carrier transport in *DNA* molecule has been developed. Tunneling and thermally induced hopping as the dominating transport mechanisms in periodic systems were included. *DNA* molecules have been estimated to operate as a switching device with the switching time as short as 10^{-14} - 10^{-13} s controlled by nucleobase sequence.

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NANO-SIZE SnO₂ FILMS DEPOSITED BY SILD METHOD: STRUCTURAL AND GAS RESPONSE CHARACTERIZATION

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The SILD (successive ionic layer deposition) technology for fabrication of nanoscaled SnO₂ films is presented. The technology allows to deposit porous agglomerated films consisting of nano-size grains. Even after annealing at 800°C the average size of crystallites does not exceed 6-7 nm. These SnO₂ films have good gas response especially to ozone and H₂.

1 Introduction

SnO₂ has been one of the most attractive metal oxides in the experimental studies during the last decades due to its gas sensor and catalysis application. Various methods were tested for deposition of SnO₂ films. They were fabricated by sputtering, sol-gel, spray pyrolysis, CVD, ALE, thermal evaporation, etc. However, not all methods are able to produce SnO₂ films with high porosity and small size of crystallites ($t < 10$ nm).

In this paper we present research on SILD technology for deposition of the mentioned above porous nanostructured SnO₂ layers. Last years the SILD technology excites high interest, because this method of metal oxide deposition is simple, inexpensive, and gives possibility to deposit thin nanostructured films on rough surfaces [1].

2 Experimental

Method of SnO₂ SILD consists of repeated successive treatments of the conductive and dielectric substrate by 0.01M solution of SnF₂, which produces poorly soluble compounds [2]. Then, samples were washed with distilled water, which removed the excess of salt, and treated with 1.5M H₂O₂ solution. After this treatment the excess of H₂O₂ was removed by heating in air at 80-100°C. The duration of each

step was 0.5 min. One cycle of the treatments comprised one deposition cycle. Si wafers and sintered quartz plates were used as substrates for SnO_2 deposition. Ellipsometric measurements testified that multiple treatments of substrates are accompanied by linear increment of film thickness. During one deposition cycle film thickness increased on 0.8-1.5 nm depending on the type of substrate [2].

For structural characterization of deposited films we used XRD, SEM, and AFM. FTIR transmission spectra were recorded at room temperature on a Perkin-Elmer-1760 spectrometer. Gas sensing characteristics were controlled using a flow-type reactor. CO (1000 ppm), H_2 (5000 ppm) and ozone (~ 1 ppm) were used as testing gases at the temperatures, corresponding to maximum gas response to reducing (425°C) and oxidizing (275°C) gases. SnO_2 films for the gas sensing studies were deposited on the quartz substrates with Ag contacts. Before measurements samples were annealed in air at 500°C for 30 min.

3 Results and discussion

Typical SEM and AFM images of surface morphology of SnO_2 films deposited by SILD method are shown in Fig. 1. The films consist of many spherical agglomerates

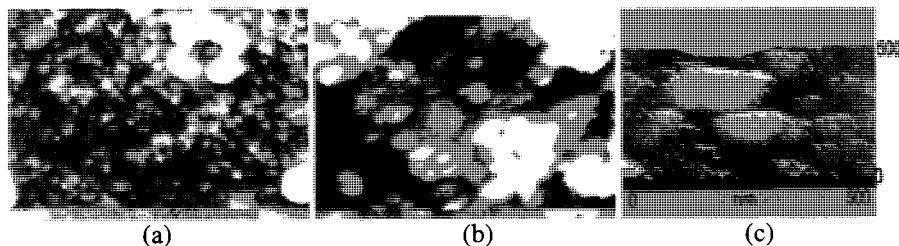


Figure 1. SEM (a,b) and AFM (c) images of SnO_2 films deposited on quartz substrate in dependence on the number of deposition cycles: a)- 20; b,c)- 40.

arranged in a porous macrostructure with very high roughness. Agglomerate size changes from 20-30 nm through 150-200 nm. SEM images clearly indicate that the size of agglomerates increases with a growth of the film thickness. This dependence is near-linear that allows to conclude the growth of the SnO_2 films to proceed through the growth of agglomerates. Films keep their porous and rough macrostructure without noticeable changes even after annealing at 800°C .

According to XRD measurements these agglomerates are fine-dispersed. We do not observe any diffraction peaks. Only after annealing at $T_{\text{an}} > 500^\circ\text{C}$ we start to observe peaks in XRD patterns, characteristic for polycrystalline material. When T_{an} increases these peaks become finer and more intense. This indicates to the growth of crystallites during the heat treatment. However, even after annealing at 800°C the size of crystallites calculated with the Scherrer formula does not exceed 6-7 nm, which is much less than the size of agglomerates (25-200 nm). Thus, there is no coalescence of crystallites forming agglomerates at this temperature.

IR spectroscopy testifies that as-deposited films are tin hydroxide or hydrated tin dioxide ($\text{Sn}(\text{OH})_4$ or $\text{SnO}_2 \cdot n\text{H}_2\text{O}$). The broad band in FTIR transmission spectra (Fig. 2a) centered around 3250 cm^{-1} is a confirmation of this conclusion. According to [3], fundamental vibration $\nu_{\text{OH}}(\text{Sn-OH})$ lies in this frequency region ($2900\text{--}3700\text{ cm}^{-1}$). The main part of coordinated water is being removed from the film already after annealing at 200°C . The changes of FTIR spectra in the region of valence Sn-O bonds ($300\text{--}700\text{ cm}^{-1}$ [3]) take place already at $T_{\text{an}} > 200^\circ\text{C}$ as well. Exactly at 200°C we observed the shift of this absorbance peak from 532 cm^{-1} to 494 cm^{-1} with postshifting to 544 cm^{-1} at 400°C , and to 583 cm^{-1} at 500°C .

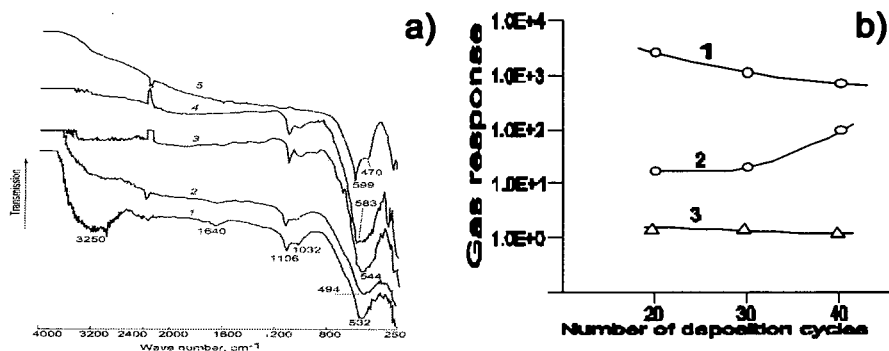


Figure 2. a) Influence of thermal treatments on the FTIR transmission spectra of SnO_2 films deposited by SILD (1-4) (40 deposition cycles) on Si substrates ($t_{\text{an}}=15\text{ min}$): 1-as-deposited films; 2- $T_{\text{an}}=200^\circ\text{C}$; 3- $T_{\text{an}}=400^\circ\text{C}$; 4- $T_{\text{an}}=500^\circ\text{C}$; 5- SnO_2 film deposited by spray pyrolysis. b) Gas response to O_3 (1), H_2 (2), and CO (3) of SnO_2 SILD films vs the number of deposition cycles.

These changes can be the result of hydroxide conversion to SnO_2 . However, in contrast to FTIR transmission spectra of SnO_2 films deposited by spray pyrolysis, we do not observe splitting of the peak in the region of $500\text{--}700\text{ cm}^{-1}$ even after annealing at 500°C . Such behavior of Sn-O absorbance peak and considerable broadening in comparison with Sn-O absorbance peak of SnO_2 polycrystalline films (20-40 nm) confirms our conclusion that the structure of SnO_2 films prepared by SILD technology is amorphous or fine-dispersed even after annealing at 500°C .

The testing of gas sensing properties of SnO_2 films deposited by SILD technology is displayed in Fig. 2b. We can assert that these SnO_2 films are gas-sensitive. The high gas response (S) is observed for both oxidizing and reducing gases. Deposited SnO_2 films have good selectivity to H_2 detection as well. The ratio $S(\text{H}_2)/S(\text{CO})$ can reach 10^2 .

As it is known, SnO_2 gas response has the chemisorption nature independently from the type of detected gas. However, we have found out that film thickness had different influence on gas response to ozone and H_2 (Fig. 2b). It testifies that different elements of gas sensing matrix control the gas response during O_3 and H_2 detection.

As we indicated earlier, the studied SnO_2 films have high gas sensitivity to H_2 . However, the gas response of SnO_2 films deposited by SILD technology is very slow. Response and recovery times during H_2 and CO detection exceed 250-300 s even at 425°C. For comparison, gas sensors on the basis of SnO_2 films deposited by spray pyrolysis at 400°C have response and recovery times equaled to 1-10 s [4]. It shows that there are additional factors limiting the speed of response of the SILD-derived SnO_2 gas sensors for detection of reducing gases. Taking into account the agglomeration structure of SnO_2 films under study one can assume that inter-crystallite diffusion is the important factor.

During ozone detection we have the other situation. Gas response to ozone is very fast. Even at 250°C the response time does not exceed 2-3 s. We can assume that during ozone detection inter-agglomerate contacts are gas sensing elements. Only in this case we can explain too fast gas response to ozone. SnO_2 films deposited by SILD have macro-porous structure, and therefore the influence of inter-crystallite diffusion can be ignored.

4 Conclusion

SILD technology gives the possibility to deposit agglomerated, porous, rough SnO_2 films with nanoscale crystallites having sizes $< 6\text{-}7$ nm. These films have high gas response to ozone and H_2 . Reaction of ozone detection is fast. The reaction of reducing gas detection is slow. We assume that inter-crystallite diffusion in agglomerates limits the speed of response of gas sensors fabricated on the basis of SILD derived SnO_2 films.

Acknowledgements

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ELECTRICAL CONDUCTIVITY AND ELECTROLUMINESCENCE OF PLANAR NANOCOMPOSITE STRUCTURES: GOLD ISLAND FILM - ALUMINUM OXYQUINOLINE

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A study of the chemical composition, structure, photo- and electroluminescent properties of a planar metal-organic nanocomposite "gold island film – Al oxyquinoline" has been performed.

1 Introduction

Nowadays much attention is given to studies of electroluminescence (EL) of semiconducting organic polymers with conjugated bonds [1]. Polymers of this kind appear to have considerable promise for elaboration of light emitting diodes. Their advantages are the ease of fabrication, the possibility to produce nanosized elements and a wider spectral range (from IR to UV) in comparison with conventional semiconductors. Almost all studies of the light emitting polymers have been made with sandwich structures, while planar systems have been investigated only in few works (see e.g. [2]).

A planar nanocomposite "gold island film – Al oxyquinoline (Alq_3)" was chosen for the present study. This organic material was taken for two reasons. First, it has a high quantum yield of photoluminescence that has been found in the experiments with sandwich structures [1]. Second, Alq_3 is a simple and rather stable polymer with conjugated bonds. It can be easily prepared by thermal vacuum deposition. Island metal films (IMFs) were selected as a component of the nanocomposite from the following considerations. It is known that the electron and photon emissions are observed when a conduction current is passed through an IMF. This emission occurs in the voltage range where the conduction current-voltage characteristic becomes superlinear. The electrons and photons are emitted from small ($\leq 0.5 \mu\text{m}$) spots called emission centers situated in the region where there exists an enhanced potential drop. The centers appear as a result of an electroforming procedure. The emission phenomena observed in IMFs can be explained by heating of the electron gas in the metal islands [3].

It was found that a region of the voltage-controlled negative differential resistance (VCNR) arises in the current-voltage characteristics as a result of adsorption of some organic molecules (naphthalene, stearone, aliphatic compounds and others) on an electroformed IMF. The bright luminescence in the VCNR region may be caused by organic molecules. The organic adsorbates used in earlier experiments [3] led to appearance of the clearly defined VCNR, but these materials have a low quantum yield of photoluminescence. This reason prompted the use of Alq_3 in the present work. Its aim was to prepare and test the electroluminescent Alq_3 nanocomposite structure of the planar type.

2 Experimental

Thin films of Al oxyquinoline (Alq_3) were prepared by thermal evaporation in vacuum. A Pt evaporator previously coated with a thin layer of Alq_3 was used. To identify the chemical composition of the Alq_3 ($(\text{C}_9\text{H}_6\text{ON})_3\text{Al}$) films deposited by this method, the IR spectroscopy was applied. The IR spectra were measured by a spectrometer IFS-66 with the Fourier transform (Bruker) in the spectral range from 4000 to 380 cm^{-1} at room temperature. An interpretation of the spectra was made on the basis of available data for the spectra of the related compounds (8-hydroquinoline, naphthalene and its substituted derivatives, etc.).

To study EL of the nanocomposite, the samples were prepared in the following way. First, the 20-30 nm Alq_3 film was deposited onto a glass substrate in vacuum. Gold film contacts of 5 mm wide separated with a gap of $30\text{ }\mu\text{m}$ were deposited onto it. The sample was mounted in a glass device with a flat window for registration of EL. The gold island film was deposited into the gap between contacts. After this, the film was subjected to the electroforming procedure. Then, the 3-5 nm Alq_3 film was deposited. The obtained composite was the object of investigation.

The structure of Alq_3 films at an early growth stage was studied in a scanning tunneling microscope (STM). The current-voltage characteristics of the local conduction current (normal to the surface) were also measured by STM in the range from -1.2 to +1.2 V. EL of the nanocomposite was recorded under a constant bias applied to the film contacts. The spectral characteristics were taken by a mirror spectrometer in the range from 400 to 650 nm.

3 Results and discussion

The reflection-absorption spectrum of an Alq_3 film deposited on Si with Au precoat shown in Fig. 1 (curve 1) is very similar to the absorption spectrum of an Alq_3 film deposited on NaCl (curve 2) and the bulk Alq_3 . A shift of the maximum of the spectral band by $1\text{-}3\text{ cm}^{-1}$ observed for the Alq_3 films on the Au precoat can be caused by an influence of the substrate local fields.

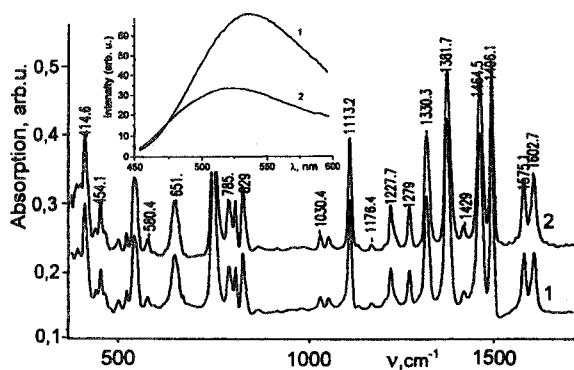


Figure 1. IR reflection-absorption and absorption spectra measured for of thin Alq_3 film deposited on Si substrate with Au precoat (1) and thin Alq_3 film deposited on NaCl substrate (2). Inset: PL spectra of thin Alq_3 film deposited on Si (1) and initial Alq_3 (2).

Consider the IR spectrum measured for the Alq_3 film obtained by the vacuum deposition. Its comparison with the spectrum of 8-hydroxyquinoline ($\text{C}_{10}\text{H}_7\text{NO}$) shows that the intense wide band caused by the stretching vibrations in the range of $3400\text{--}2200\text{ cm}^{-1}$ is absent in the Alq_3 spectrum. This testifies that there are no hydroxyl groups in the deposited Alq_3 , i.e. its molecular structure is maintained. The bands in the $3100\text{--}3030\text{ cm}^{-1}$ range correspond to the stretching vibrations of $\text{q}(\text{CH})$ aromatic rings observed in the spectra of all related compounds, such as quinoline, naphthalene and its substituted derivatives. The characteristic bands recorded in the vibrational spectra of the evaporated Alq_3 films correspond to those in the spectra of bulk Alq_3 . Thus, it is reasonably safe to suggest that the chemical composition of the deposited films corresponds to the initial bulk Alq_3 .

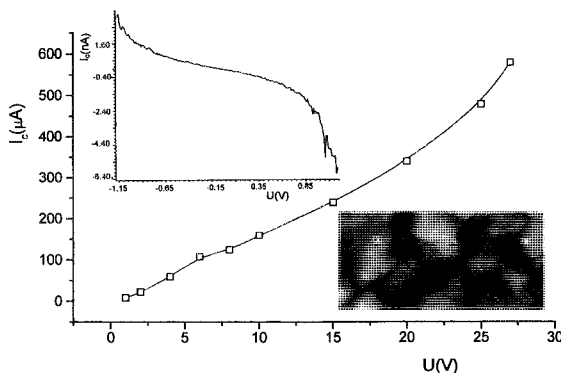


Figure 2. Current-voltage characteristic of the nanocomposite "island gold film – Alq_3 " measured along the surface. Bottom inset: STM image of 4 nm Alq_3 film on mica substrate covered with 30 nm gold film. Upper inset: Local STM conduction current-voltage characteristic of a separate block of the Alq_3 film.

The Alq_3 film at its initial growth stage (thickness of a few nm) is shown to consist of blocks of 4–5 nm thickness and several tens of nanometers in horizontal size (Fig. 2, inset). An example of the current-voltage curve of the local conduction current measured in STM normal to the surface is presented in Fig. 2 (upper inset).

The shape of the curve is symmetrical relative to the polarity of the applied voltage, and it becomes superlinear at 0.5–0.6 V. The light emission under the STM tip is observed at ~ 1.5 V that corresponds to the local electric field strength $\sim 3 \cdot 10^6$ V/cm.

Fig. 2 shows also the conduction current-voltage curve of the nanocomposite gold island film – Alq₃ measured along the surface. The light and electron emission are observed at ~ 15 V when this curve becomes superlinear. The light emission stems from discrete centers located along the gap between contacts. The EL spectrum of this nanocomposite is given in Fig. 3. The highest band of the light emission is seen at ~ 520 nm, which is typical for Alq₃. The gold islands also radiate in the investigated spectral range, which results in a complex shape of the EL spectrum of the nanocomposite.

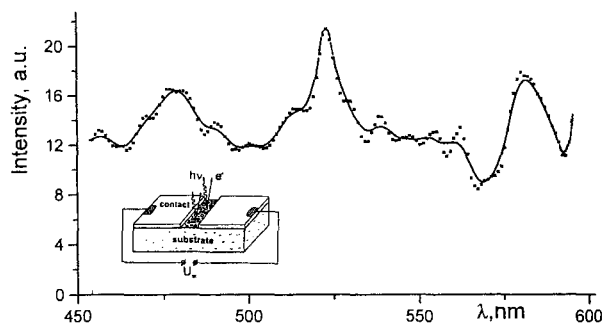


Figure 3. The light emission spectrum of the nanocomposite “island gold film – Alq₃” under applied voltage of 22 V. The inset shows a schematic of the planar structure.

Thus, the important feature of the planar light emitting structures based on the nanoisland films is the possibility to govern their EL spectra using the contribution from both organic component and nanoparticles.

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TEXTURED POROUS SILICON FOR EFFICIENT LIGHT DETECTION IN UV, VIS AND NIR SPECTRUM RANGES

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Advanced porous silicon (PS) based structures for a light detection in UV, VIS and NIR ranges are discussed. PS in light detectors is shown to enhance significantly the photoresponse and to decrease the reflectance of the structures promoting more efficient device operation. The surface of PS being highly texturized enhances light trapping and reduces reflection losses. Formation of the PS layer from pyramidal-film texture facilitate efficient light trapping. The tunability of the PS bandgap may be used to optimize the sunlight absorption.

1 Introduction

Silicon is the most promising material for light sensing devices. It would hence be of great importance if conventional Si technology could be applicable for the fabrication of light sensing devices to be on-chip integrated with a silicon electronic IC. The challenge of effective thin film Si light detectors consists of four major tasks: (i) the formation of a high quality shallow p-n junction at the silicon wafer surface; (ii) the incorporation of a light trapping layer to compensate for the intrinsically weak absorption of crystalline silicon; (iii) an effective passivation of surfaces, and (iv) the formation of a good optical image with improved absorption profile.

Much attention is presently devoted to porous silicon (PS) in the context of application to light sensing devices. Bandgap broadening, absorption spectrum in the range of 0.8 - 1.3 eV, very good optical transmission by wavelength 700 - 1000 nm [1] and photoconductivity [2] imply utilization of PS in silicon light detectors. Innovative film textures such as pyramidal-film texture [3] facilitate efficient light trapping.

In this study, an advanced textured PS/Si structure for the light detection in ultraviolet, visible and near infrared ranges is discussed.

2 Experimental

A p-type, 10^{18} cm^{-3} boron doped, (100)-oriented monocrystalline Si wafer was subjected to anisotropic chemical etching in 10% KOH at 80°C for 5-30 min to produce inverted 1.0-1.5 μm pyramids at the period of 1.5-2.0 μm . The pyramidal-film textured surface was transformed into a 1.5 μm thick PS layer by anodising in the aqueous 12% HF solution at the current density of 30 mA/cm^2 . Phosphorus ions were implanted through the PS layer at 50 keV, $6 \cdot 10^{11} \text{ cm}^{-2}$. A subsequent rapid thermal processing at 1000°C for 30 s formed shallow n^+ -p junction at the interface between the PS layer and the Si substrate.

Photoresponse spectra of n^+ -p structures were measured in the spectral range of 280-1100 nm under short circuit current conditions.

3 Results and discussion

Fig. 1 shows the spectral response of light detectors formed in the textured PS/Si structure in comparison to the spectral response of the devices fabricated in the pyramidal-film Si wafer without PS. The use of PS in light detectors significantly enhances the photoresponse.

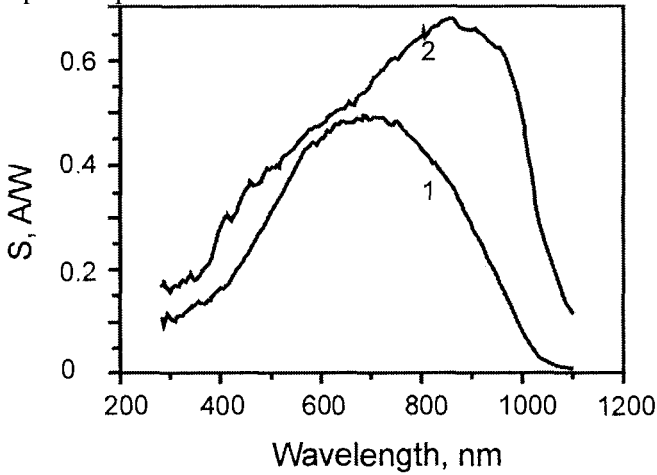


Figure 1. Photoresponse spectra of the light detectors: 1 - textured PS/Si structure; 2 - pyramidal-film Si wafer without PS.

Fig. 2 shows the spectral dependence of the reflection index for the above structure. Using PS in light detectors decreases the reflectance of the structures promoting more efficient device operation.

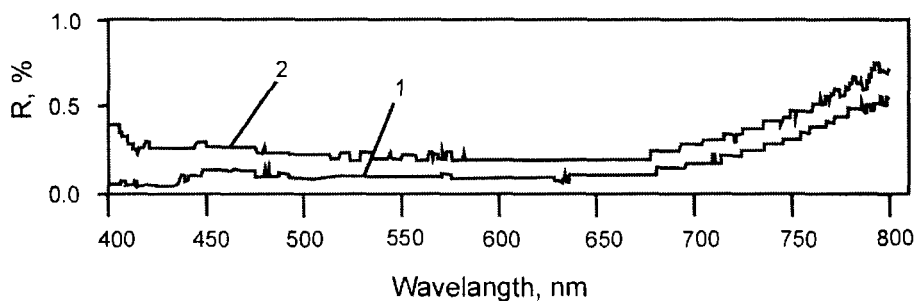


Figure 2. Spectral dependence of the reflection index for: 1 - textured PS/Si structure; 2 - pyramidal-film Si wafer without PS.

Thus, the surface of PS being highly texturized enhances light trapping and reduces reflection losses. The tunability of the PS bandgap may be used to optimize the sunlight absorption. In addition, the porous structure allows easy dopant introducing through the top PS layer into the surface of the underlying Si wafer to create a shallow p-n junction. The wide bandgap of PS may qualify it as a window layer in the PS/Si tandem structure.

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RELAXATION PROCESSES IN RARE EARTH DOPED CRYSTALS AS STUDIED BY HIGH RESOLUTION FOURIER SPECTROSCOPY

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Experimental method and the theoretical approach developed to study relaxation processes in rare-earth doped crystals are briefly outlined on the examples of $\text{Er}^{3+}:\text{LiYF}_4$ and $\text{Pr}^{3+}:\text{CsCdBr}_3$. Possible applications to nanostructured materials are discussed.

1 Introduction

Thin film structures doped with luminescent lanthanides are of primary interest for optoelectronics. In most cases, lanthanides enter solid state in the form of trivalent ions, Ln^{3+} . Optical 4f electrons of Ln^{3+} ions are well shielded by the outer $5s^2$ and $5p^6$ filled electron shells, so that the lines of optical transitions remain relatively narrow even in condensed matter. A reach energy spectrum of $4f^n$ configuration results in a possibility to observe absorption (emission) of Ln^{3+} -doped solids in a wide spectral range extending from the far-infrared via visible to ultraviolet region. In particular, the infrared luminescence of Er^{3+} at about $1.5\ \mu\text{m}$ (corresponding to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition) falls into a maximum transparency window of optical fibers. Much work has been done to incorporate lanthanides, Er in particular, into silicon-based optoelectronic materials. Promising results on an intensive Er-luminescence have been obtained from porous Si coated by sol-gel derived xerogel films (see, e.g., [1]). However, the tree-like nonregular configuration of pores in mesoporous silicon leads to a non-reproducible Er-luminescence intensity [1]. The use of regular porous structures of anodic alumina [2] has allowed to considerably improve the parameters of luminescent Ln^{3+} -containing films [3]. Strong enhancement of Er and Tb luminescence from xerogel films confined in mesoporous anodic alumina has been reported recently [4]. In contrast to lanthanide-doped semiconductor films, a strong reduction of concentration quenching was observed.

To further improve characteristics of lanthanide-based optoelectronic materials, it is important to study the nature of luminescent centers in them, the interaction of

optical electrons with the matrices (in particular, with atomic vibrations), the relaxation processes. In the present paper we show that the method of optical Fourier-transform spectroscopy offers new possibilities in studying infrared transitions of Ln^{3+} ions, in comparison with other spectroscopic techniques (Section 2). Our research on Er^{3+} in LiYF_4 presents an example what information on relaxation processes can be extracted from the spectra (Section 3). An important effect of an essential redistribution of the phonon density of states in solids doped with lanthanide ions is discussed in connection with our work on $\text{Pr}^{3+}:\text{CsCdBr}_3$ (Section 4).

2 Fourier-transform spectroscopy

2.1 Fundamentals

The principal parts of a Fourier-transform spectrometer (FTS) are the Michelson interferometer with a moving mirror (see Fig.1) and a computer that performs the Fourier transform of the interferogram and thus calculates the spectrum of an incident radiation $E(t)$. A detector registrates the averaged intensity at the output of the Michelson interferometer

$$\Phi(t) \sim \overline{[E(t) + E(t+\tau)]^2} = \overline{E^2(t)} + \overline{E^2(t+\tau)} + 2\overline{E(t)E(t+\tau)}. \quad (1)$$

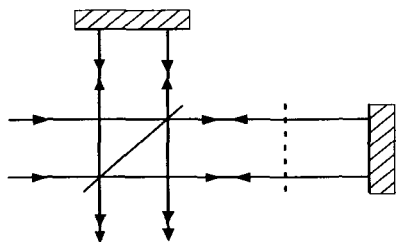


Figure 1. Scheme of the Michelson interferometer.

Here $\tau=l/c$ is the time delay between the two interfering beams, l being the path difference. Under certain conditions, that usually are fulfilled, the first two terms in (1) are equal to the time-independent mean intensity while the third term represents the autocorrelation function

$$\psi(\tau) = \overline{E(t) \cdot E(t+\tau)} \quad (2)$$

which depends on the time delay τ . The Fourier transformation of $\psi(\tau)$ yields the spectrum, namely,

$$B(\omega) = \frac{2}{\pi} \int_0^\infty \psi(\tau) \cos \omega \tau d\tau. \quad (3)$$

A real instrument delivers $\psi(\tau)$ for the interval $[0, L/c]$, where L is the maximum path difference which depends on the maximum displacement of the moving mirror of the FTS. The L -dependent instrumental function, that is the response of an instrument to a monochromatic incident light $E(t) = \cos \omega_0 t$, can be written as

$$f_L = \frac{1}{\pi} \frac{\sin(\omega - \omega_0)L/c}{(\omega - \omega_0)}. \quad (4)$$

$f_L \rightarrow_{L \rightarrow \infty} \delta(\omega - \omega_0)$, where $\delta(\omega - \omega_0)$ is the delta-function; for a finite L , f_L exhibits secondary maxima, the distance between the first zeroes of f_L , $\delta\omega = 2\pi c/L$, or, in wavenumbers, $\delta\sigma = 1/L$, characterizes the spectral resolution. The free spectral range $\Delta\sigma$ for the FTS depends on a number N of points registered in the interferogram:

$$\Delta\sigma = N\delta\sigma \quad (5)$$

Typically, $N \sim 10^6$, so even for high resolution ($\delta\sigma \sim 10^{-3} \text{ cm}^{-1}$) instruments $\Delta\sigma \sim 10^3 \text{ cm}^{-1}$, and thus broad-band high-resolution spectroscopy is possible with FTS.

FTS analyses all the spectral elements simultaneously which results in the so called Fellgett or multiplex advantage of FTS over conventional instruments in signal-to-noise ratio. For the intensity-independent noise of a detector (infrared spectral region) the Fellgett advantage is maximum, namely, $\sqrt{M}$, where $M = \Delta\sigma/\delta\sigma$ is the number of registered spectral elements. Additional gain comes from a large throughput of a FTS in comparison with a slit spectrometer (Jacquinot advantage). In Fourier transform spectroscopy, the wavenumber scale is established relative to the frequency of a stabilized laser used for the measurement of the path difference and, as a result, is precise in the whole spectral region (Connes advantage). General advantages of the FTS over conventional instruments make them a useful tool for material research.

In particular, it is advantageous to register by FTS a weak absorption (as in the case of lanthanide ions in films or nanostructures).

2.2 Experimental setup

In our research, we used a BOMEM DA3.002 Fourier-transform spectrometer equipped with a controlled-temperature ($\pm 0.1 \text{ K}$ in the range between 2 and 300 K) helium-vapor cryostat. High-resolution (up to 0.005 cm^{-1}) spectra were registered in the spectral range between 2000 and 11000 cm^{-1} .

3 Relaxation processes in $\text{Er}^{3+}:\text{LiYF}_4$

The scheelite crystal LiYF_4 doped with Er^{3+} ion is well known as an efficient multifrequency laser material. Laser actions at 2.7 and $1.5 \mu\text{m}$ that occur between the $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ and, respectively, $^4\text{I}_{13/2}$ and $^4\text{I}_{15/2}$ multiplets have attracted particular interest because of applications in optical fiber lines and medicine.

Spectra corresponding to the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$ transitions are presented in Fig. 2. The main goal of our high-resolution work on $\text{Er}^{3+}:\text{LiYF}_4$ [5] was to compare the experimentally measured linewidths with the calculated ones and thus to check the validity of the previously developed theoretical model of the electron-phonon interaction [6] for calculation of phonon relaxation rates.

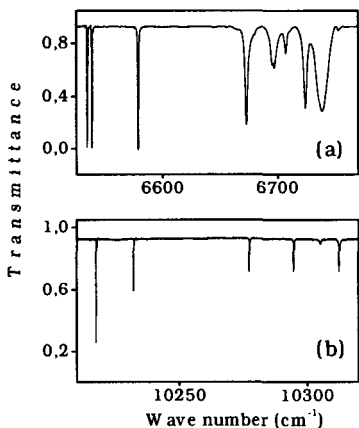


Figure 2. Transmittance spectra of LiYF₄:Er³⁺ (0.2%) at 5 K in the region of the transitions (a) ⁴I_{15/2}→⁴I_{13/2} and (b) ⁴I_{15/2}→⁴I_{11/2}. E,HLLc polarization.

The crystal-field Hamiltonian is represented by the expression

$$H_{cf} = \sum_{p,k} B_p^k C_p^k, \quad (6)$$

where C_p^k are irreducible tensor operators and B_p^k are crystal-field parameters. The electron-phonon interaction comes from the change of crystal-field parameters due to displacements of atoms from their equilibrium positions in the lattice. In linear approximation it can be written as follows:

$$H_{el-ph} = \sum_{s\alpha} V_\alpha(s) [u_\alpha(s) - u_\alpha(Er)];$$

$$V_\alpha(s) = \sum_{pk} B_{p,\alpha}^k(s) C_p^k, \quad (7)$$

where $\mathbf{u}(s) - \mathbf{u}(Er)$ is the difference between dynamic displacements of the ligand ion s and the Er³⁺ ion, $\alpha = x, y, z$, and $B_{p,\alpha}^k(s)$ are the coupling constants. The latter can be calculated in the framework of a model giving an explicit expression of crystal-field parameters on distances between a Ln³⁺ ion and other ions in the lattice. We use here the exchange charge model [6] to calculate the coupling constants and crystal-field levels and wavefunctions.

The probability of the one-phonon transition between the electronic initial (i) and final (f) states with energy gap $\hbar\omega_{if} > 0$ can be presented as

$$W_{if} = \frac{2}{\hbar} \sum_{s\alpha\beta} \langle f | V_\alpha(s) | i \rangle \text{Im} g_{\alpha\beta}(ss' | \omega) \langle i | V_\beta(s') | f \rangle \times [n(\omega_{if}) + 1] \quad (8)$$

where $n(\omega)$ is the phonon occupation number and $g_{\alpha\beta}(ss' | \omega)$ are the linear combinations of the lattice Green's functions for the differences between displacements of ligands and the Er³⁺ ion [5]. We performed a calculation of the relaxation rates for all the crystal-field sublevels within the manifolds of ⁴I_{11/2} and

$^4I_{13/2}$ multiplets. Frequencies and polarization vectors of phonons in the LiYF₄ crystal were obtained at 8000 points in the irreducible part of the Brillouin zone using the rigid ion model of lattice dynamics derived on the basis of neutron scattering data. Matrix elements of electronic operators $V_a(s)$ were calculated with the wave functions obtained from the crystal-field calculation. The inverse lifetimes of the crystal-field sublevels determine the widths of corresponding absorption lines.

$$1/\tau_i = W_i = \sum_f W_{if} \quad (9)$$

Despite many simplifying approximations there is a good agreement between the measured linewidths and the estimated relaxation rates [5] (see Table 1).

4 Redistribution of the phonon density of states in activated crystals: $\text{Pr}^{3+}:\text{CsCdBr}_3$.

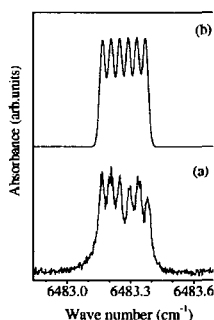


Figure 3. (a) Measured hyperfine structure with resolution of 0.005 cm^{-1} and (b) calculated hyperfine structure of the $^3H_4(^1\Gamma_1) \rightarrow ^3F_3(^1\Gamma_3)$ transition of $\text{CsCdBr}_3:\text{Pr}^{3+}$.

A further development of the displayed approach to the electron-phonon interaction and relaxation processes in crystals activated by lanthanide ions came from the high-resolution study of $\text{Pr}^{3+}:\text{CsCdBr}_3$ [7]. These crystals have recently attracted a considerable interest being a promising material for up-conversion lasers due to the property of their quasi-one-dimensional lattice to incorporate Ln^{3+} ions in pairs.

Resolved hyperfine structure (hfs) due to the interaction of optical electrons with the magnetic moment of the Pr nucleus ($I=5/2$) was observed in the spectra (Fig. 3). The measured hyperfine splittings and widths of hyperfine sublevels found from the experimental line shapes are presented in Table I.

Even at the liquid-helium temperature the hfs of the most of excited crystal-field sublevels is masked by the spontaneous relaxation broadening. Strong electron-phonon interaction effects in $\text{CsCdBr}_3:\text{Ln}^{3+}$ crystals originate from the specific density of phonon states that has large maxima in the low-frequency region ($20\text{--}40 \text{ cm}^{-1}$) in the perfect crystal lattice (see Fig. 4 and Ref. [8]).

We performed a calculation of the relaxation rates using the phonon Green's functions of the perfect (CsCdBr_3) and locally perturbed (impurity dimer centers in $\text{CsCdBr}_3:\text{Pr}^{3+}$) crystal lattices obtained in Ref. [8]. The formation of a dimer leads to a strong perturbation of the crystal lattice (mass defects in the three adjacent Cd^{2+} sites and large changes of force constants). As it has been shown in Ref. [8], the local spectral density of phonon states essentially redistributes and several localized modes appear near the boundary of the continuous phonon spectrum of the

Table 1. Measured linewidths in the absorption spectra [5,7] and calculated one-phonon transition probabilities in $\text{LiYF}_4\text{:Er}^{3+}$ and $\text{CsCdBr}_3\text{:Pr}^{3+}$ ($T=5$ K).

$\text{LiYF}_4\text{:Er}^{3+}$				$\text{CsCdBr}_3\text{:Pr}^{3+}$			
Multiplet, CF level	E, cm^{-1}	$W, 10^{10} \text{ s}^{-1}$		Multiplet, CF level	E, cm^{-1}	$W, 10^{10} \text{ s}^{-1}$	
		experiment	theory			experiment	theory
$^4\text{I}_{11/2} \Gamma_{78}^{(3)}$	10312	0.35	0.30	$^3\text{F}_3 \Gamma_3^{(2)}$	6503	5.85	4.2
$\Gamma_{78}^{(2)}$	10306	0.76	0.41	Γ_1	6496	3.20	0.80
$\Gamma_{56}^{(3)}$	10295	0.21	0.44	$\Gamma_3^{(1)}$	6483	0.75 ^a	0.13
$\Gamma_{56}^{(2)}$	10277	0.20	0.76	$^3\text{F}_2 \Gamma_1$	5153	52.8	30.9
$\Gamma_{56}^{(1)}$	10232	0.018	0.007	$\Gamma_3^{(2)}$	5148	-	19.4
$\Gamma_{78}^{(1)}$	10218	0.016	-	$\Gamma_3^{(1)}$	5073	0.94 ^a (1.32 ^b)	0
$^4\text{I}_{13/2} \Gamma_{56}^{(4)}$	6738	7.0	6.22	$^3\text{H}_5 \Gamma_3^{(4)}$	2620 ^c	-	52.0
$\Gamma_{78}^{(3)}$	6724	2.7	2.58	$\Gamma_2^{(2)}$	2593 ^c	-	77.5
$\Gamma_{56}^{(3)}$	6696	2.5	4.11	$\Gamma_3^{(3)}$	2547	13.2	18.2 ^d
$\Gamma_{78}^{(2)}$	6672	2.0	2.89	Γ_1	2332	62.2	48.7
$\Gamma_{56}^{(2)}$	6579	0.07	0.10	$\Gamma_3^{(2)}$	2317	56.6	116.4
$\Gamma_{56}^{(1)}$	6538	0.017	0.0003	$\Gamma_3^{(1)}$	2261	5.65 (6.4 ^b)	1.9
$\Gamma_{78}^{(1)}$	6534	0.015	-	$\Gamma_2^{(1)}$	2235	0.94 ^a	0

^a - inhomogeneous width

^b - total width of the unresolved hyperfine structure

^c - calculated crystal field energy

^d - two-phonon relaxation rate

unperturbed lattice. As an example of changes in the phonon spectrum, spectral densities $D_{\alpha\alpha}(\omega)$ of displacement-displacement autocorrelation functions

$$\langle u_{\alpha}^2(R) \rangle = \int D_{\alpha\alpha}(\omega) d\omega \quad (10)$$

in the perfect ($R=\text{Cd}^{2+}$) and perturbed ($R=\text{Pr}^{3+}$) lattices at zero temperature are shown in Fig. 4. Calculated inverse lifetimes are given in Table I. It is seen that there is a good correlation between the measured linewidths and the relaxation rates obtained with the perturbed Green's functions. Calculations with Green's functions of the perfect lattice gave overestimated (up to an order of magnitude higher) values of relaxation rates. Thus, we conclude that the increased Pr^{3+} -ligand elastic interaction, as compared to the Cd^{2+} -Br⁻ interaction, and corresponding enhancement of correlations between displacements of the impurity Ln^{3+} ion and its neighbors strongly suppress the electron-phonon coupling.

It should be noted that the measured width of the doublet $^3\Gamma_3(^3\text{H}_5)$ is 5 times larger than the estimated total hfs width, though the one-phonon relaxation broadening of this level is not possible at low temperatures. We suppose that this level, and two upper levels $^2\Gamma_2(^3\text{H}_5)$ and $^4\Gamma_3(^3\text{H}_5)$ are essentially broadened due to the two-phonon relaxation. Two-phonon relaxation rates were calculated taking into

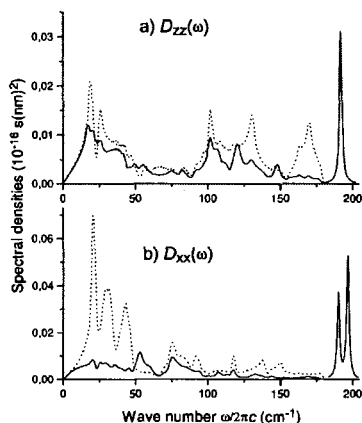


Figure 4. Simulated spectral densities of displacement-displacement autocorrelation functions for Cd^{2+} in CsCdBr_3 (dotted curves) and for Pr^{3+} in the impurity dimer centers (solid curves).

account linear and quadratic terms in the electron-phonon interaction Hamiltonian and were found to be dominated by the second-order contribution from the linear electron-phonon interaction. The localized modes that appear in an activated crystal contribute essentially to the two-phonon relaxation rates.

5 Conclusion

We have performed high-resolution study of line widths and line shapes in Ln^{3+} -doped crystals. To analyze the experimental data, the theoretical approach was used based on a realistic model of the lattice dynamics and crystal-field parameters and electron-phonon coupling constants calculated in the framework of the exchange charge model. The most essential results of this work are the following.

- One- and two-phonon relaxation rates between levels of a Ln^{3+} ion embedded into a solid matrix can be satisfactorily described by the above mentioned theoretical approach.
- Redistribution of the phonon density of states due to local deformations caused by an introduction of an impurity Ln^{3+} ion is of primary importance for electron-phonon interaction effects. In particular, for $\text{Pr}^{3+}:\text{CsCdBr}_3$ the effective electron-phonon coupling is *strongly suppressed* due to a local increase of elastic forces in the activated crystal and the corresponding enhancement of correlation between displacement of the impurity Ln^{3+} ion and its neighbors.

When dealing with nanostructured materials, it is important to take into account a suppression of the low-frequency part of the phonon density of states due to confinement effects. This circumstance in parallel with phonon bottleneck effects due to additional selection rules in anharmonic decay of high-frequency matrix excitations may result in a reduction of relaxation rates for Ln^{3+} ions in nanostructures and in an appropriate enhancement of lanthanide luminescence in

them. Fourier-transform luminescent spectroscopy of Ln^{3+} ions in nanostructured materials under a selective excitation could be useful for an experimental verification of this hypothesis.

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